



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
WATER

JUL 2 1987

MEMORANDUM

SUBJECT: Pretreatment Program Guidance

FROM: James R. Elder, Director
Office of Water Enforcement
and Permits (EN-335)

TO: Users of the Guidance Manual for
Preventing Interference at POTWs

This guidance manual was developed by EPA to aid publicly owned treatment works (POTWs) in identifying, tracking, and mitigating interference episodes caused by discharges of nondomestic wastes. Interference is defined in the General Pretreatment Regulations (40 CFR Part 403) in terms of a discharge which, alone or in combination with other discharges, inhibits or disrupts the POTW and causes it to violate its NPDES permit or applicable sludge use or disposal regulations. The legal responsibilities of POTWs and their industrial users for avoiding interference are specified in the General Pretreatment Regulations. The basic regulatory requirements are explained in this manual and technical guidance is provided to help POTW operators detect and determine the sources of interference.

This document will be useful to all POTWs that may experience interference problems, not just those that have been required to establish federally-approved pretreatment programs. Therefore, EPA is distributing it widely. Additional copies of this guidance manual or further information about the national pretreatment program can be obtained by writing to the Permits Division, (EN-336), US EPA, 401 M St., S.W., Washington, D.C. 20460.

001609

EPA is preparing another guidance document that deals specifically with the development of local limits to prevent interference and pass through. It was distributed in draft form for comment to States and EPA Regions in May 1987 and will be mailed to all POTWs with federally-approved pretreatment programs when final. Additional information about the local limits guidance document can also be obtained from the Permits Division.

2.1.1 Chronic Inhibition

Chronic inhibition refers to a more or less consistent pattern of impairment of the functioning of the biomass in a biological treatment process caused by influent pollutant concentrations that are above tolerable levels. Inhibition is usually defined by a decrease in oxygen uptake rate or a decrease in COD/BOD removal. If the inhibition leads to a permit violation, it then is classified as interference. This type of interference results from either a continuous or semi-continuous discharge of an industrial pollutant to the POTW. Chronic inhibition may also result from the total effect of several industries discharging a variety of inhibitory pollutants. Industrial sources of chronic problems tend to be by-products of production activities such as chemical derivatives, rinse waters and contact cooling water.

The effects of an inhibitory pollutant on plant biomass vary depending on how frequently and at what level the pollutant is discharged. The more consistently a pollutant is fed to the biological treatment process, the more chance the biomass has to develop a "resistance" to the pollutant. If a pollutant is fed at a fairly even rate and concentration, the biomass will generally eventually become accustomed to or "acclimate" to the pollutant, and BOD removal efficiency will no longer suffer. For this reason, a plant may experience operational problems unless there has been sufficient time for the biomass to become acclimated. In addition, discharges of toxics at high enough concentrations can cause inhibition even in acclimated systems.

Although it does not always result in a POTW violating its NPDES permit limits, chronic inhibition can increase the overall expense and difficulty of operating a treatment plant in compliance with NPDES permit limits. For example, a plant may have to be operated at an increased MCRT or require additional aeration capacity to counteract the negative effects of inhibition. Depending on the circumstances, this may involve significantly increased operating costs for recirculating sludge at a higher rate or providing more aeration. It may also take away any reserve capacity that the plant might otherwise have had for future growth. Therefore, POTW's experiencing chronic inhibition should take steps to mitigate it even when there is no immediate threat of an NPDES permit violation.

2.1.2 Upset Conditions

The results of 29 case studies performed in conjunction with the development of this manual showed that most interference problems are caused by intermittent discharges of high-strength conventional wastes which overload a POTW's organic capacity, causing plant upset. The term "upset" is used in this manual to refer to an exceptional incident which creates a temporary non-compliance with permit limits due to the impacts of the incoming waste characteristics on the treatment processes. Discharges causing upset commonly come from food processors such as bakeries, dairies, breweries, canneries, poultry farms and meat packaging plants. Examples of interferences due to high-strength conventional wastes are provided by the Bayshore Regional Sewerage

001610





Contribution from the Department of Chemistry,
Miami University, Oxford, Ohio.

Iron(III)-Catalyzed Decomposition of the Chlorite Ion: An Inorganic Application of the Quenched Stopped-Flow Method

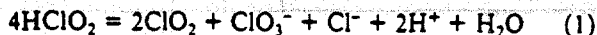
István Fábián* and Gilbert Gordon*

Received July 30, 1991

The kinetics and mechanism of the iron(III)-catalyzed decomposition of the chlorite ion have been investigated by using conventional batch, stopped-flow, stopped-flow-rapid-scan spectrophotometric, and quenched stopped-flow methods at 25 °C and in 1.0 M NaClO₄. The concentration vs time profiles were determined for chlorite ion, chlorine dioxide, and, in a few cases, chloride ion in the 40 ms–several minute interval. It was confirmed that the stoichiometry can be given as the appropriate combination of the following reactions: $4\text{HClO}_2 = 2\text{ClO}_2 + \text{ClO}_3^- + \text{Cl}^- + 2\text{H}^+ + \text{H}_2\text{O}$; $5\text{HClO}_2 = 4\text{ClO}_2 + \text{Cl}^- + \text{H}^+ + 2\text{H}_2\text{O}$. The proposed mechanism postulates that the catalytic decomposition is initiated by the formation of the FeClO_2^{2+} complex and the rate-determining step is the redox decomposition of this species. The mechanism was validated by model calculations based on the GEAR algorithm. The measured and calculated kinetic curves are in excellent agreement under a variety of experimental conditions. It was shown that the overall stoichiometry is kinetically controlled and ultimately determined by fast secondary reactions between various chlorine species. This work represents the first totally inorganic application of the quenched stopped-flow method. Several aspects of this technique are discussed.

Introduction

In aqueous solution, the disproportionation of the chlorite ion¹ exhibits complex stoichiometric and kinetic patterns.² The stoichiometry is kinetically controlled³ and can be expressed as a linear combination of eqs 1 and 2.



The rate of disproportionation is significantly enhanced by various inorganic and organic species. This was frequently utilized in chlorite ion based oscillation reactions⁴ or in other systems showing exotic kinetic phenomena.⁵

Ferric ion catalyzes the ClO_2^- decomposition.^{6–8} On the basis of spectrophotometric experiments, Schmitz and Rooze⁸ reported the stoichiometry to be consistent with reaction 1 and concluded that the reaction order with respect to chlorite ion, ferric ion, and chlorine dioxide is 2, 1, and –1, respectively.

Recently, we have investigated the same system in the sub-second region by using stopped-flow (SF) and stopped-flow-rapid-scan spectrophotometric (SF-RS) methods. The formation⁹ of FeClO_2^{2+} ($K = 13.8 \text{ M}^{-1}$) was found to be fast and kinetically coupled with the decomposition of the chlorite ion. Chlorine dioxide formation was observed in significant amounts in a few hundred milliseconds after mixing the reactants. The formation of the FeClO_2^{2+} complex, which is not included in the Schmitz and Rooze mechanism, as well as the fast initial steps is of crucial kinetic importance in the overall mechanism.

In this study, the kinetics of the iron(III)-catalyzed chlorite ion decomposition were investigated by using a combination of conventional batch, SF, SF-RS, and quenched stopped-flow (QSF) experiments. This appears to be the first totally inorganic application of the QSF method.¹⁰ It provides direct information for the concentration vs time profiles of the reactants and products in the sub-second time domain. These data and our recent results⁹ can serve to develop and verify a detailed mechanism for the decomposition of ClO_2^- under a wide range of experimental conditions. At the same time, we expect that the results will contribute to our understanding of the chemistry of the chlorite ion.

Experimental Section

Chemicals. The recrystallization of NaClO₂ from commercially available sodium chlorite (OLIN; approximately 80% purity) and the preparation of the iron(III) stock solutions were described earlier.^{9,11,12} Chloroacetic acid was twice recrystallized from 95% ethanol. All other chemicals, sodium fluoride and formate (Matheson Coleman & Bell) and sodium acetate and perchloric acid (Fisher), were of the highest com-

mercially available grade and were used without further purification. The concentrations of ClO_2^- , Fe^{3+} , and the pH were varied in ranges 0.001–0.25 M, 5.0×10^{-5} – 5.0×10^{-3} M, and 1.0–4.5, respectively. The ionic strength was adjusted to 1.0 M with sodium perchlorate prepared from Na₂CO₃ (Fisher) and HClO₄. The temperature was 25.0 ± 0.05 °C in all experiments.

Conventional Kinetic Measurements. The reaction was triggered by adding small aliquots of acidic Fe^{3+} solution to vigorously stirred (900 rpm) solutions. The reaction mixture was immediately transferred in a tightly sealed cuvette, and the spectra were recorded on a Hewlett-Packard 8450 UV–visible diode array spectrophotometer. Measurements were made in both the presence and the absence of acetate, formaldehyde, and chloroacetate buffer. The pH of the samples was either calculated on the basis of the appropriate equilibrium data (pH < 2.3) or measured with a Radiometer GK2401B combination glass electrode attached to a Radiometer PHM64 pH meter. The electrode was calibrated such that the pH-meter reading directly gave the hydrogen ion concentration ($[\text{H}^+]$).

Stopped-Flow Measurements. The reaction was followed with an Atago Bussan/Photol Otsuka Electronics RA-401 stopped-flow instrument attached to an RA-451 data processor unit. The SF and SF-RS traces were monitored with a Hamamatsu R374 photomultiplier and a 512-channel diode array detector, respectively. The SF traces were taken as the average of at least five replicate runs. In these experiments the base line was set to 0.0 absorbance with 1.0 M NaClO₂; thus, the results can be compared directly to other spectrophotometric data.

Stoichiometry. At various reaction times, 25-cm³ aliquots of the reaction mixture were mixed with 1 cm³ of 0.5 M NaF solution and pH was set between 3.3 and 3.7 by adding appropriate amount of chloroacetate buffer. Thus, iron(III) was completely converted to catalytically inactive fluoro complexes and the decomposition was stopped. Since the final pH was relatively high, the uncatalyzed decomposition of the chlorite ion was also quenched. In a carefully sealed cuvette the spectra of the samples did not change over more than 15–20 min.

001611

- (1) Chlorite ion and chlorous acid are in fast acid–base equilibria and present in a concentration ratio determined by the actual pH. In this paper, the two species will be distinguished only when it is required for the clarity of the presentation.
- (2) Gordon, G.; Kieffer, R. G.; Rosenblatt, D. H. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1983; Vol. 15, pp 201–286.
- (3) Kieffer, R. G. *J. Am. Chem. Soc.* 1968, 90, 235.
- (4) Epstein, I. R.; Orban, M. In *Oscillations and Traveling Wave Chemical Systems*; Field, R. J., Burger, M., Eds.; Wiley: New York, 1985; pp 257–286.
- (5) De Kepper, P.; Boissonade, J.; Epstein, I. R. *J. Phys. Chem.* 1990, 94, 6525 and references therein.
- (6) Launer, H. F.; Wilson, W. K.; Flynn, J. *J. Am. Chem. Soc.* 1953, 75, 237.
- (7) Launer, H. F.; Tomimatsu, Y. *J. Am. Chem. Soc.* 1954, 76, 2.
- (8) Schmitz, G.; Rooze, H. *Can. J. Chem.* 1984, 62, 2231; 1985, 63, 191.
- (9) Fábián, I.; Gordon, G. *Inorg. Chem.* 1991, 30, 3002.

Table I. Typical Stoichiometric Results from Conventional Kinetic Studies for the Iron(III)-Catalyzed Chlorite Ion Decomposition^a

time, min	$10^3 C_{ClO_2^-}$, M	$10^3 C_{ClO_2}$, M	$10^3 C_{Cl^-}$, M	$\Delta C_{ClO_2^-}/C_{ClO_2}$	C_{ClO_2}/C_{Cl^-}	av oxidn no. ^b
0	10.42					3.00
2.0	8.12	1.34	0.52	1.72	2.53	3.01
4.0	7.53	1.66	0.71	1.74	2.32	2.98
10.0	6.20	2.17	0.96		2.25	
15.0	4.76	2.44	1.08	1.73	2.27	2.96
20.0	4.12	3.20	1.40	1.77	2.28	2.97
30.0	3.64	3.52	1.55	1.79	2.28	2.99
45.0	3.05	3.69	1.62	1.73	2.28	3.01
	2.39	3.91	1.81	1.88	2.16	3.00
	2.39	4.21	1.95	1.90	2.16	3.02

^a Conditions: $C_{ClO_2^-} = 1.04 \times 10^{-2}$ M, $C_{Fe^{3+}} = 8.52 \times 10^{-4}$ M, $C_{HCOONa} = 0.040$ M, $C_{HClO_4} = 0.030$ M. ^b Average oxidation number = $(3C_{ClO_2^-} + 4C_{ClO_2} + 5C_{ClO_3^-} - C_{Cl^-})/C_{ClO_2^-}$.

This time interval was sufficiently long to analyze the reaction mixture by various methods.

Fluoride ion forms very stable nonabsorbing complexes with iron(III),^{13,14} and the concentrations of ClO_2^- and ClO_2 could be determined without interference by using the HP spectrophotometer. In a few cases, the total concentration of these two species was determined by using an iodometric method¹⁵ in order to verify the spectrophotometric results. The titrations were made with a Radiometer ABU93 Triburette autoburette station which was connected to a Radiometer VIT90 Video Titrator unit equipped with a standard P101 platinum-K401 SCE electrode pair (Radiometer).

The chloride ion concentration was determined by potentiometric titrations with 0.002 M $AgNO_3$ solution in 70% methanol using a P101 platinum-F1012Cl chloride ion selective electrode pair (Radiometer).¹⁶ Because of the relatively low concentration levels of chloride ion, the $\pm 2.0\%$ error of these titrations was higher than usual. The difference between the concentration of initially added ClO_2^- and the sum of the concentrations of ClO_2 , ClO_2^- , and Cl^- was attributed to the chlorate ion. On the basis of this assumption, the calculated average oxidation number is in excellent agreement with the theoretical value of 3 (cf. Table I). This confirms that other chlorine species and/or oxygen is not formed in significant concentrations.

Quenched Stopped-Flow Experiments. The QSF measurements were made with a Hi-Tech Scientific Model PQ-53 Preparative Quencher. The basic concepts of this method and the details of the experiments will be discussed in the next section.

Results

Kinetic runs without added iron(III) confirmed that the contribution of the uncatalyzed pathway to the overall decomposition of chlorite ion sharply decreases by increasing the pH. The importance of the uncatalyzed pathway was found to be minimal even at the lowest pH and iron(III) concentrations applied in this study.

Figure 1 shows the typical spectral change observed in the presence of the catalyst. The absorbance increase at 360 nm is primarily attributed to chlorine dioxide formation. In the 230–280-nm region, the net effect of the disappearance of chlorite ion and the formation of ClO_2 is observed. In particular, in the far-UV region, various iron species also may have some contribution to the observed spectra.^{17,18} The spectral changes indicate that, after a relatively fast initiation period, the decomposition markedly slows down.

The same general kinetic profile was found under a variety of experimental conditions. However, in the presence of buffers, the decomposition rate decreases. This is most likely the result of complex formation between iron(III) and the buffer, which decreases the concentration of the catalytically active iron species.

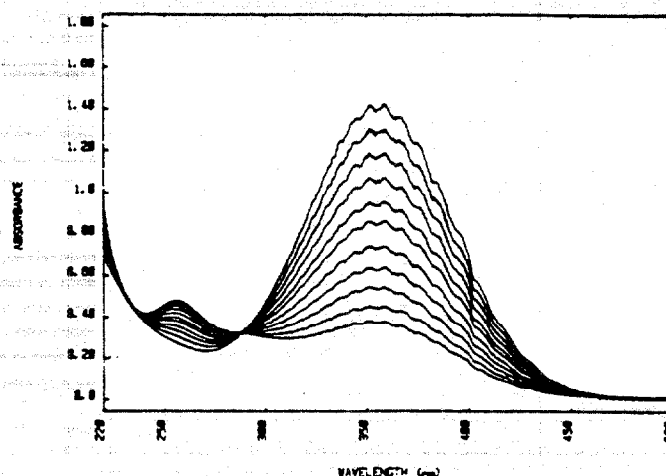


Figure 1. Typical absorption spectra for the iron(III)-catalyzed decomposition of chlorite ion as a function of time (0.5-cm cell). $C_{ClO_2^-} = 5.20 \times 10^{-3}$ M, $C_{Fe^{3+}} = 1.10 \times 10^{-3}$ M, and pH = 2.40. In the order of increasing absorbance at 360 nm, the spectra were recorded 20, 30, 50, 80, 140, 240, 360, 600, 1000, 1800, and 4000 s after mixing the reactants. Dotted line: spectrum of Fe(III) at the same pH.

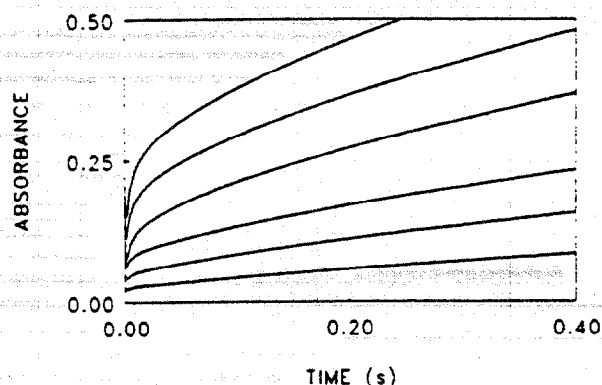


Figure 2. Selected stopped-flow traces recorded in a 10-mm cell for the iron(III)-catalyzed decomposition of chlorite ion at 370 nm. $C_{ClO_2^-} = 9.93 \times 10^{-3}$ M and $C_{HClO_4} = 6.67 \times 10^{-3}$ M. In increasing order of the absorbance, $C_{Fe^{3+}}$ for these curves is 5.51×10^{-3} , 1.38×10^{-4} , 2.75×10^{-4} , 5.51×10^{-4} , 8.26×10^{-4} , and 1.10×10^{-3} M.

In acetate, formate, or chloroacetate buffer, the decay of the reaction rate by increasing pH shows good correlation with the formation of the corresponding iron(III) monocomplex.¹³

In the absence of buffers, the decomposition rate varies only slightly with pH in the 1.0–2.3 region. However, at higher pH values and at longer reaction times, the absorbance slowly decreases in the 360-nm region. Also, larger than expected absorbance changes are observed around the 260-nm maximum of the chlorite ion. These spectral observations are attributed to hydrolytic reactions of iron(III). The formation of polynuclear iron species is typically associated with slow spectral changes in the UV region.¹⁷

Chloride ion strongly affects both the stoichiometry and kinetics of the uncatalyzed disproportionation of chlorite ion.^{3,19} In the present study, replicate kinetic runs were carried out by varying chloride ion concentrations up to 0.1 M. The corresponding near-UV-visible spectra were identical within the experimental limitations. However, in the far-UV region, the absorbance invariably was slightly higher in the presence of chloride ion. The observed deviations are consistent with the formation of strongly absorbing iron(III) chloro complexes at low concentration levels. These measurements also confirmed that the product chloride ion has at most marginal kinetic effect on the catalytic decomposition process.

A typical data set for the stoichiometry of the decomposition is shown in Table I. The concentration ratios of the reacted chlorite ion and the products clearly indicate that reaction 1 alone

- (13) (a) Sillén, L. G.; Martell, A. E. *Stability Constants*; Chemical Society: London, 1964; Supplement No. 1, 1971. (b) *Stability Constants of Metal-Ion Complexes, Part A: Inorganic Ligands*; Högföldt, E., Ed.; IUPAC Chemical Data Series No. 21; Pergamon Press: Oxford, U.K., 1982.
- (14) Pouli, D.; Smith, W. M. *Can. J. Chem.* 1960, 38, 567.
- (15) Gordon, G.; Tachiyashiki, S. *Environ. Sci. Technol.* 1991, 25, 468.
- (16) Tang, T.-F.; Gordon, G. *Environ. Sci. Technol.* 1984, 18, 212.
- (17) Milburn, R. M.; Vosburgh, W. C. *J. Am. Chem. Soc.* 1955, 77, 1352.
- (18) Popa, G.; Luca, C.; Iosif, E. *Z. Phys. Chem. (Leipzig)* 1963, 222, 49.

- (19) Kieffer, R. G.; Gordon, G. *Inorg. Chem.* 1968, 7, 239.

001612

is not sufficient to characterize the stoichiometry. This finding is in contradiction with the results of Schmitz and Rooze.⁸ Since these authors did not report the details of their experiments, we could not trace the source of the discrepancy. According to our data, only the combination of reactions 1 and 2 can properly describe the observed concentration ratios. In this respect, the catalytic decomposition is analogous to the uncatalyzed reaction. It should be added that the stoichiometry varies slightly with the actual concentrations and it also appears to change to some extent within a given kinetic run.

Typical SF traces at 370 nm are shown in Figure 2. Since neither ClO_2^- nor the catalyst solutions have significant absorbance at 370 nm, the sharp increase at the very beginning of these curves corresponds to the very fast formation of one or more new species. In the first 15–20 ms, the rate of the absorbance change is consistent with the formation of FeClO_2^{2+} . However, other species also may contribute to the overall spectral effect. Even with the initial region ignored, the SF traces reflect composite kinetic features. The experimental data could not be interpreted in terms of a simple rate law.

The interplay of various kinetic effects also was observed at 510 nm, where the primary absorbing species⁹ is FeClO_2^{2+} . The complex formation is rapid, and FeClO_2^{2+} is in pseudoequilibrium with chlorite ion. Accordingly, as the decomposition proceeds and the chlorite ion concentration decreases, steadily decaying absorbance curves are expected. At lower chlorite ion concentrations the SF traces were consistent with this expectation. However, the absorbance change was reversed by increasing the initial concentration of ClO_2^- . This observation probably can be interpreted in terms of massive chlorine dioxide formation. ClO_2 is characterized by a very weak absorbance at 510 nm. Still, at high concentration levels, its increasing contribution to the measured absorbance overcompensates the disappearance of the FeClO_2^{2+} complex.

The fast kinetic measurements presented here and reported earlier provide ample kinetic information concerning the initial part of the decomposition reaction. In general, the observed spectral changes reflect simultaneous concentration changes of ClO_2^- , HClO_2 , ClO_2 , $\text{Fe}(\text{OH})^{2+}$, FeClO_2^{2+} , and possible other iron(III) species. In addition, the equilibria between the corresponding acid–base pairs are continuously repositioned during the reaction, depending on the actual stoichiometry involving the hydrogen ion. In the absence of buffers, this latter problem is eliminated, but additional side reactions, such as complex formation with the buffer, offset this advantage.

In principle, the experimental data can be evaluated by using advanced fitting procedures and the concentration vs time profiles can be calculated for each component. However, considering the complexity of the present system coupled with the experimental limitations, the integrity of the results from such calculations is questionable. For example, among the various components, chlorine dioxide has the most characteristic spectrum and the most reliable concentrations are expected for this species. In this context, preliminary evaluation of the data by using a nonlinear least-squares routine²⁰ gave somewhat ambiguous concentrations even for ClO_2 .

The application of the QSF method offers a possibility of determining the concentration vs time profiles for the reactants and products. This fast kinetic technique was developed primarily for studying biochemical reactions which are not associated with characteristic spectral changes.²¹

The QSF method has not been generally applied in kinetic studies of inorganic reactions. The schematic of the instrument applied in this study is shown in Figure 3. Basically, the QSF method consists of two stopped-flow sequences which are electronically controlled and monitored. First, drive I is activated and the studied reaction is triggered by fast mixing of the reactants in mixer I. By the end of this stage, the reaction tube is filled

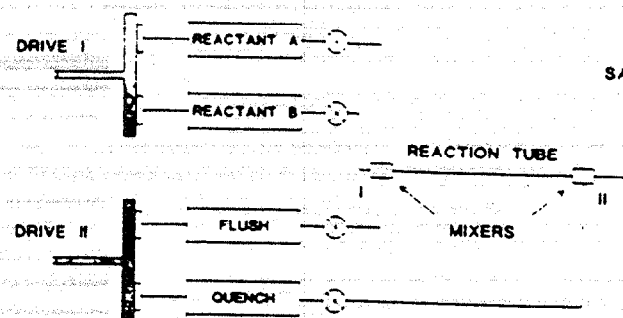


Figure 3. Schematic of the quenched stopped-flow instrument.

with the reaction mixture. After a certain incubation period, II is activated. The reaction tube is flushed in order to force reaction mixture out of the aging tube. Generally, 1.0 M NaF is used in order to reduce the corrupted end-zone of the reaction plug. The flush solution also contains NaF at relatively concentration levels to quench the catalytic effect of any unreacted iron(III). Immediately following the flush, the reaction mixture is chemically stopped by injecting the quench reagent into the reaction mixture (mixer II). The collected samples can be conveniently analyzed by a variety of techniques.

Providing that the quench reaction is extremely fast, the average of the quenched reaction mixture (t_q) is given by eq 3, w

$$t_q = V_T(t_I/V_R + t_{II}/V_Q)/2 + t_d$$

V_T , V_R , V_Q , t_I , t_{II} , and t_d are the volumes of the reaction tube, delivered reaction mixture, and quench solution, the duration of drives I and II, and the time delay between the two SF quenches, respectively. In order to obtain uniformly aged samples, the speed of the two drives has to be synchronized such that $t_I = t_{II}/V_Q$. As a result of a detailed calibration, the reproducibility of the delivered volumes of the reactants and the quench and flush solutions as well as their flow rates is $\pm 1.5\%$. With the actual configuration, the cumulative dead time (the shortest t_d) was ~ms.

In the stoichiometric experiments, fluoride ion effectively stopped the catalytic decomposition of ClO_2^- , and the contribution of fluoro complexes to the measured spectra was negligible. The formation kinetics of the iron(III) monofluoro complex was investigated in 0.02–0.4 M perchloric acid by Pouli and Smit. On the basis of the activation parameters given by these authors, the estimated forward rate constant for the $\text{Fe}^{3+} + \text{F}^- \rightleftharpoons \text{FeF}^{2+}$ step is $5.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. With this rate constant, calculated lifetime of free iron(III) would be ~3 ms in 0.05 M F^- solution. In less acidic solutions, i.e. at pH > 2.0, a much faster complex formation is expected because ligand substitution reactions of iron(III) are much faster²² via $\text{Fe}(\text{OH})^{2+}$ than via Fe^{3+} . Stopped-flow measurements in the Fe^{3+} – F^- system were consistent with this expectation.

The ability of fluoride ion to quench the decomposition was further tested in SF-RS experiments by mixing solutions of ClO_2^- and F^- with iron(III) solution. No chlorine dioxide formation was observed in these experiments, indicating that, for all practical purposes, the catalyst was instantaneously deactivated. Since fluoride ion acts as a buffer ($\text{p}K_a = 2.95^{13}$) and increases the pH above 2.7, the uncatalyzed decomposition also was stopped. On the basis of these results, fluoride ion was used as quencher in 0.1 M or higher concentrations in the QSF measurements.

In the first set of QSF experiments, the quenched samples were diluted in formate buffer and analyzed as detailed in the Experimental Section. As seen in Table II, the results are consistent with the stoichiometric studies at longer times of the reaction. It should be noted that, in the initial part of the reaction, the experimental error in the chlorite ion determination is comparable with its concentration change. Therefore, only the $[\text{ClO}_2^-]/[\text{ClO}_2]$

(20) Fábián, I. Private communication. NESSIE: A General Purpose Non-Linear Least Square Fitting Program; Debrecen, Hungary, 1982.

(21) Barman, T. E.; Travers, F. *Methods Biochem. Anal.* 1985, 31, 1.

Margerum, D. W.; Cayley, G. M.; Pagenkopf, C.; Pagenkopf, K. In *Coordination Chemistry*; Martell, A. E., Ed.; American Chemical Society: Washington, DC, 1978; Vol. 2, pp 1–220 and references therein.

Table II. Typical Stoichiometric Results from Quenched Stopped-Flow Studies for the Iron(III)-Catalyzed Chlorite Ion Decomposition^a

Time, s	$10^3 C_{\text{ClO}_2^-}$, M	$10^3 C_{\text{ClO}_2}$, M	$10^3 C_{\text{Fe}^{3+}}$, M	$C_{\text{ClO}_2}/C_{\text{ClO}_2^-}$
0	10.03			
0.01	10.05	0.63	0.30	2.14
0.02	10.04	1.01	0.42	2.38
0.03	9.91	1.67	0.66	2.53
0.04	9.85	2.36	1.02	2.31
0.05	9.60	3.09	1.26	2.45
0.06	9.60	3.66	1.34	2.75
0.07	9.44	4.19	1.67	2.51
0.08	9.46	4.56	1.65	2.76
0.09	9.40	5.00	1.82	2.65
0.10	9.19	5.59	1.98	2.82
0.12	9.02	5.98	2.17	2.79

^a Conditions: $C_{\text{ClO}_2^-} = 0.100$ M, $C_{\text{Fe}^{3+}} = 8.26 \times 10^{-4}$ M, $C_{\text{HClO}_4} = 9 \times 10^{-2}$ M; quencher 0.25 M NaF.

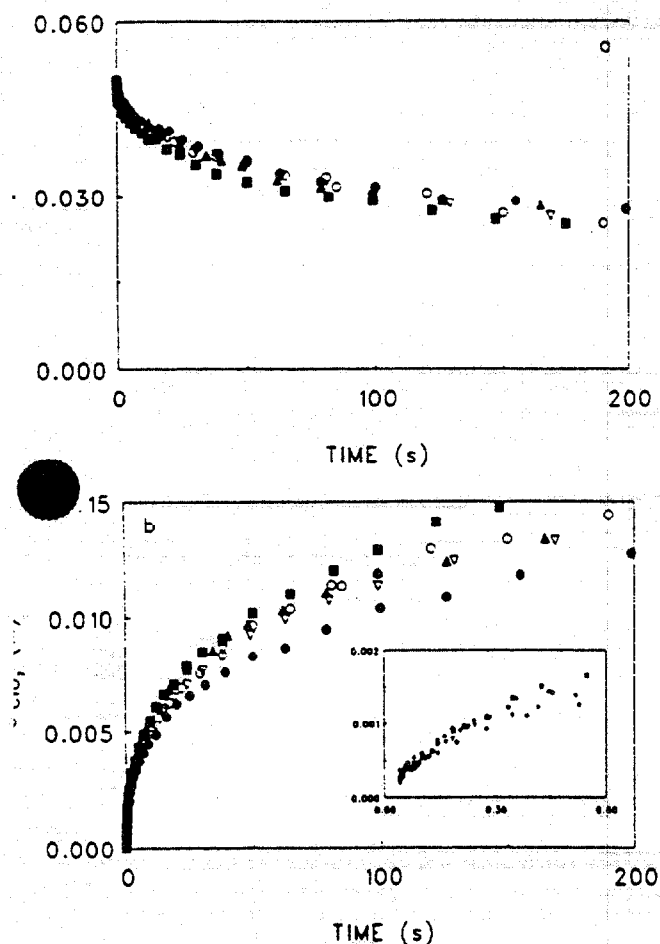


Figure 4. Concentration vs time profiles obtained from the quenched stopped-flow experiments for chlorite ion (a) and chlorine dioxide (b) as a function of the pH. Insert: enlarged first portion of the same curves. $C_{\text{ClO}_2^-} = 4.99 \times 10^{-2}$ M and $C_{\text{Fe}^{3+}} = 1.39 \times 10^{-3}$ M. pH: 1.25 (●); 1.50 (○); 1.75 (■); 2.00 (□); 2.25 (▲).

Concentration ratio should be considered to be a reliable indicator of the stoichiometry.

Typical kinetic curves are shown in Figures 4 and 5. These figures, as well as Table II, demonstrate that otherwise unavailable quantitative information could be obtained by using the QSF method. Most importantly, the concentration vs time profiles for chlorite ion were obtained directly for the initial part of the

agreement with the results from conventional kinetic measurements, the reaction rate exhibits negligible pH dependence in the pH 1.25–2.25 range. The disappearance of chlorite ion and the formation of chlorine dioxide show analogous kinetic patterns over the entire time domain, each indicating the autoinhibitive character of the decomposition. This observation can be ration-

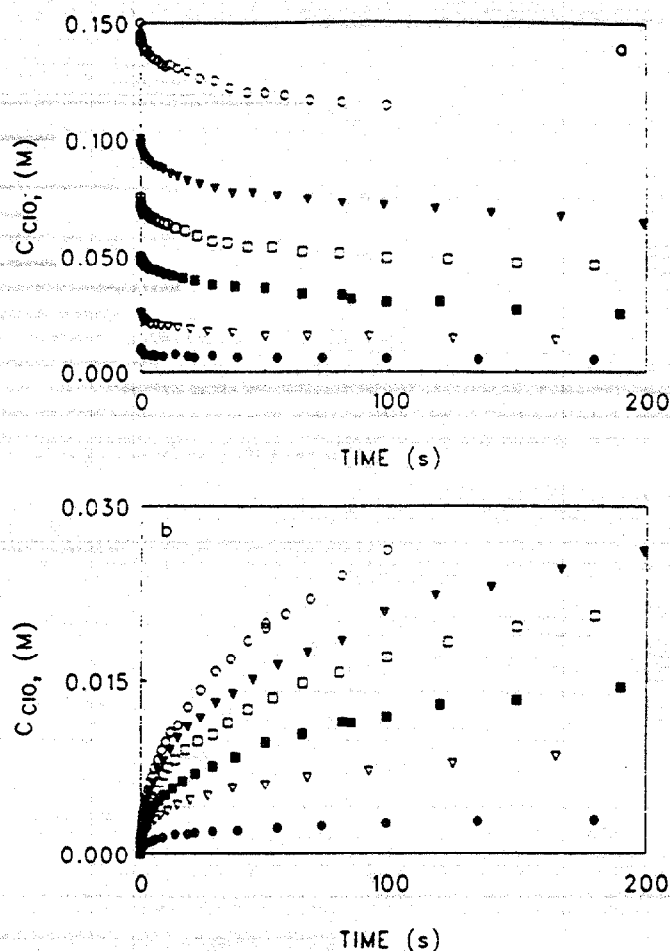


Figure 5. Concentration vs time profiles obtained from the quenched stopped-flow experiments for chlorite ion (a) and chlorine dioxide (b) as a function of the chlorite ion concentration. pH = 1.75 and $C_{\text{Fe}^{3+}} = 1.39 \times 10^{-3}$ M. $C_{\text{ClO}_2^-}$: 9.99×10^{-3} M (●); 2.50×10^{-2} M (○); 4.99×10^{-2} M (■); 7.50×10^{-2} M (□); 9.99×10^{-2} M (▼); 0.150 M (○).

Table III. Comparison of Conversions in QSF Experiments and in an Open Reactor after 3-min Reaction Time^a

pH	$10^3 C_{\text{Fe}^{3+}}$, M	% reacted chlorite ion	
		QSF exp ^b	open reactor
1.25	1.40	43.3	57.2
1.50	1.40	47.4	63.3
1.75	1.40	48.5	71.6
2.00	1.40	50.0	68.6
1.75	2.79	45.2	79.9
1.75	4.19	54.0	83.6

^a $C_{\text{ClO}_2^-} = 0.100$ M. ^b Interpolated values.

alized by assuming either the steady removal of the catalytically active iron(III) species or, as suggested by Schmitz and Rooze,⁸ a mechanism in which the product ClO_2 inhibits the decomposition. In order to distinguish between the two possibilities, several QSF runs were repeated in an open reactor by continuously purging the reaction mixture with N_2 . This method was sufficient to remove substantial amounts of chlorine dioxide, though the efficiency was not quantified. In spite of the semiquantitative nature of these experiments, the comparison of the corresponding conversion data at the same reaction time (Table III) proves that more chlorite ion decomposed in the open reactor; i.e., the inhibition is probably associated with chlorine dioxide formation.

Discussion

The Mechanism. A detailed kinetic model for the catalytic decomposition of ClO_2^- is summarized in Table IV. As a result of our SF studies, we propose that the catalytic decomposition is initiated by complex formation between chlorite ion and iron(III). The intrinsic mechanism for the FeClO_2^{2+} formation includes fast protolytic equilibria between the corresponding

001614

base pairs and the ligand substitution steps with Fe^{3+} and $\text{Fe}(\text{OH})^{2+}$ (the first five reactions in Table IV).⁹ The SF experiments also confirmed that the redox decomposition of the FeClO_2^{2+} complex competes with its formation, and the value of 30.1 s^{-1} was estimated for the corresponding first-order rate constant. Two alternatives can be envisioned for the decomposition:

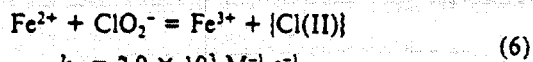


Direct experimental evidence appears to be unattainable to distinguish the two possible pathways. However, reaction 4 can be rejected on the basis of the following arguments.

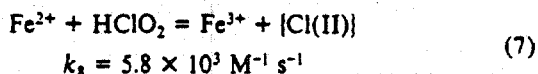
The FeClO_2^{2+} complex shows intense absorbance in the visible region. Similar to those of other iron(III) complexes, this spectral feature is assigned to a ligand to metal charge-transfer band. Accordingly, one electron of the ligand is partially shifted toward the metal center, making more favorable the decomposition via reaction 5 than that via reaction 4. An analogous internal oxidation-reduction pathway was suggested for the decomposition of the $\text{Co}(\text{NH}_3)_5\text{ClO}_2^{2+}$ complex by Thompson.²³

The fact that chlorine dioxide was observed in the very early phase of the reaction also suggests that reaction 5 is the main pathway of the decomposition. If FeClO_2^{2+} decomposed by means of reaction 4, chlorine dioxide production would start only in a subsequent step between Cl(II) and presumably chlorite ion. Thus, an incubation period would be expected in the concentration vs time profiles for ClO_2 . No such incubation period was observed.

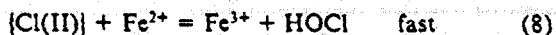
In the presence of strong oxidizing agents, such as chlorite ion or chlorine dioxide, iron(II) is rapidly converted into iron(III). For the oxidation of Fe^{2+} by chlorite ion, the mechanism shown in eqs 6–8 was proposed by Ondrus and Gordon²⁴ (since the exact



$$k_7 = 2.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$



$$k_8 = 5.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$$



composition of the transient species is not known, these equations were not balanced).

The transient chlorine(II) species is extremely reactive and is in steady state. Thus, a simple two-term second-order rate law, shown in eq 9, can be derived for the overall oxidation process.

$$v = (k_7[\text{ClO}_2^-] + k_8[\text{HClO}_2])[\text{Fe}^{2+}] \quad (9)$$

Under our experimental conditions, chlorite ion is in 10^3 – 10^4 -fold excess over iron(II). In addition, the reactions between ClO_2^- and lower oxidation state chlorine species, with the exception of Cl^- , are generally fast.^{11,25} Accordingly, a fast reaction can be envisioned between the chlorine(II) intermediate and chlorite ion (reaction 10) which is superior to reaction 8 and replaces it in the Ondrus–Gordon mechanism.



For the reaction sequence of eqs 6, 7, and 10, the rate law and stoichiometry are given by eqs 9 and 11, respectively. In principle,



the product HOCl is in fast acid–base equilibrium with ClO^- ($\text{p}K_a \sim 7.5$).¹³ However, in the applied pH region, this equilibrium is completely shifted to HOCl and need not be considered in the mechanism.

Iron(II) is also oxidized by the product chlorine dioxide, and as the reaction proceeds, this pathway becomes increasingly significant. The oxidation may occur in a single outer-sphere step or in an inner-sphere process, which implies that reaction 5 is reversible. Since the two alternative pathways are experimentally

indistinguishable and give equivalent interpretations of the data, in further discussions only the inner-sphere mechanism will be considered. At this point, it should be emphasized that the forward rate constant for reaction 5 was estimated on the basis of SF experiments in the first 40–50 ms of the overall reaction where the contribution of ClO_2 to the oxidation of Fe^{2+} is presumably small but not necessarily negligible. According to the estimated value for k_5 , appears to be reliable only within a factor of 2–3.

By using the corresponding standard electrode potentials, Schmitz and Rooze⁸ estimated the equilibrium constant for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{ClO}_2/\text{ClO}_2^-$ redox couples in 1.0 M NaCl at 25°C : $K = [\text{ClO}_2][\text{Fe}^{2+}]/([\text{ClO}_2^-][\text{Fe}^{3+}]) = 2.7 \times 10^{-4}$. On the basis of this value and the stability constant of the FeClO_2^{2+} complex, K_6 was calculated to be $2.0 \times 10^{-5} \text{ M}$. On the basis of the equilibrium constant and $k_6 = 30.1 \text{ s}^{-1}$, $1.5 \times 10^6 \text{ M}^{-1} \text{ s}$ obtained for k_4 . Obviously, these values are only as good as the equilibrium and kinetic parameters used for their estimation. While the standard electrode potential for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple appears to be well established ($\epsilon^\circ = 0.771 \text{ V}$), there is considerable ambiguity in the value for the $\text{ClO}_2/\text{ClO}_2^-$ couple. For example, the standard electrode potential used by Schmitz and Rooze ($\epsilon^\circ = 0.935 \text{ V}$) is 133 mV less than the value recently recommended by Bratsch²⁶ ($\epsilon^\circ = 1.068 \text{ V}$). Earlier electrode potentials for the $\text{ClO}_2/\text{ClO}_2^-$ couple suggest even larger divergence.²⁷ A 13% variation in the electrode potential results in more than a 2-fold variation in the magnitude of K_6 and k_4 .

At longer times, the ClO_2 concentration increases as a result of oxidation of Fe^{2+} by chlorite ion becomes less important compared to reaction 5. The chlorine dioxide production decreases, and the system approaches an equilibrium state, which is primarily determined by the complex formation and reaction 5. This interpretation is consistent with the inhibitive feature of the overall reaction. It should be added that, in various redox reactions of oxychlorine species, ClO_2 is one of the final products and does not react with other chlorine species. Therefore, no chemically acceptable pathway can be envisioned for the chlorine dioxide inhibition in the present system.

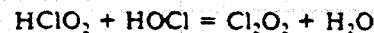
Additional steps of the mechanism include the reaction of hypochlorous acid, formed in reaction 11, with chlorite ion. This reaction has been investigated under a variety of experimental conditions.^{11,15,16,25,28,29} It is generally agreed that higher reactant concentrations, lower pH, and chlorite ion excess favor the formation of chlorine dioxide over chlorate ion. In acidic solution, the hypochlorous acid–chlorite ion reaction is extremely fast and probably does not become rate determining in the chlorite ion decomposition. As a consequence, hypochlorous acid can accumulate in this system and is in steady state. Nevertheless, a precise kinetic model for the $\text{HOCl}-\text{ClO}_2^-$ reaction is not available because the final stoichiometry is determined by the delicate balance between the two competing pathways leading to the formation of ClO_2 and ClO_3^- .

With a few modifications, the mechanism proposed by Peacock et al.¹¹ was adopted for the $\text{HOCl}-\text{ClO}_2^-$ reaction. Similar to other kinetic models, this mechanism postulates the formation of a reactive Cl_2O_2 intermediate.



$$k = 1.1 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$$

By taking into account the protonation of chlorite ion as a pre-equilibrium, one can rewrite eq 12 in the following form:



$$k_{10} = 2.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$$

Rate constant k_{10} is calculated by using $\text{p}K_a = 1.72$ for chlorous acid.

(23) Thompson, R. C. *Inorg. Chem.* 1979, 18, 2379.

(24) Ondrus, M. G.; Gordon, G. *Inorg. Chem.* 1972, 11, 985.

(25) Emmenegger, F.; Gordon, G. *Inorg. Chem.* 1967, 6, 633.

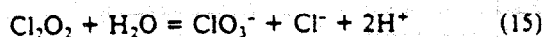
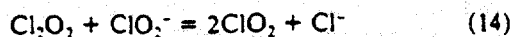
(26) Bratsch, S. G. *J. Phys. Chem. Ref. Data* 1989, 18, 1.

(27) Latimer, W. *Oxidation Potentials*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952.

(28) Taube, H.; Dodgen, H. J. *Am. Chem. Soc.* 1949, 71, 3330.

(29) Aicita, E. M.; Roberts, P. V. *Environ. Sci. Technol.* 1986, 20, 5.

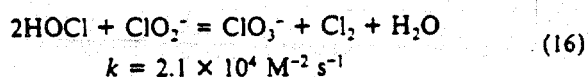
The following two steps were justified for the Cl_2O_2 intermediate:



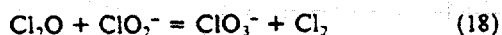
the rates of these reactions have different concentration dependencies, the corresponding rate constants could not be determined, only their ratio: $k_{11}/k_{12} = 5.4 \times 10^4 \text{ M}^{-1}$. The Cl_2O_2 intermediate is presumably in steady state; i.e., reactions 14 and 15 should be considerably faster than reaction 13. In order to maintain this condition, $k_{11} = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{12} = 9.3 \times 10^3$ were used for the calculations.

In the reaction between chloride ion and hypochlorous acid, chlorine is formed, which in turn reacts with chlorite ion¹¹ ($k_{14} = 3.7 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$). For the Cl^- -HOCl step, the rate constants reported by Eigen and Kustin³⁰ were accepted without modifications.

Peintler et al. also found some evidence for another third-order reaction step and suggested that it occurs via a preequilibrium¹¹ between ClO_2^- and HOCl:



We propose an alternative interpretation of reaction 16, which includes the formation of chlorine monoxide:

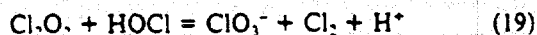


Although the formation of chlorine monoxide in aqueous solution and an equilibrium constant for reaction 17 were reported by Roth³¹ as early as 1929, this species has not been included in previous mechanisms for the HOCl- ClO_2^- reaction. Kinetic data related to reaction 17 indicated that it is catalyzed by hydrogen ion and acetic acid.³²⁻³⁴ According to a recent report by Beach and Margerum,³⁴ the equilibrium constant (K_{15}) and the forward rate constants for the uncatalyzed (k_{15}) and acetic acid catalyzed pathways are $1.15 \times 10^{-2} \text{ M}^{-1}$, $0.12 \text{ M}^{-1} \text{ s}^{-1}$, and $80 \text{ M}^{-2} \text{ s}^{-1}$, respectively. The forward rate constant for the hydrogen ion catalyzed pathway³² (k_{16}) is $3.1 \text{ M}^{-2} \text{ s}^{-1}$.

The comparison of the rate constants for the oxidation of the $\text{Si}(\text{CN})_4^{2-}$ complex by Cl_2O , Cl_2 , and HOCl demonstrated³⁴ that chlorine monoxide is the most reactive among these species. If this reflects a general trend, chlorine monoxide may have a central role in the HOCl- ClO_2^- reaction.

Under the experimental conditions applied by Peintler et al.,¹¹ reaction 17 can be regarded as a fast preequilibrium. On the basis of this approximation, rate constant k_{17} is calculated to be $1.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

The mechanism for the HOCl- ClO_2^- reaction is complete with an additional step recently proposed by Gordon and Tachiyashiki:¹⁵



As a starting point in the calculations, we use the same rate constant for this step as for reaction 11, i.e. $k_{18} = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

Calculations. In order to validate the mechanism, concentration vs time profiles were simulated by using a GEAR algorithm³⁵ based program (ZITA)³⁶ and compared with the experimental

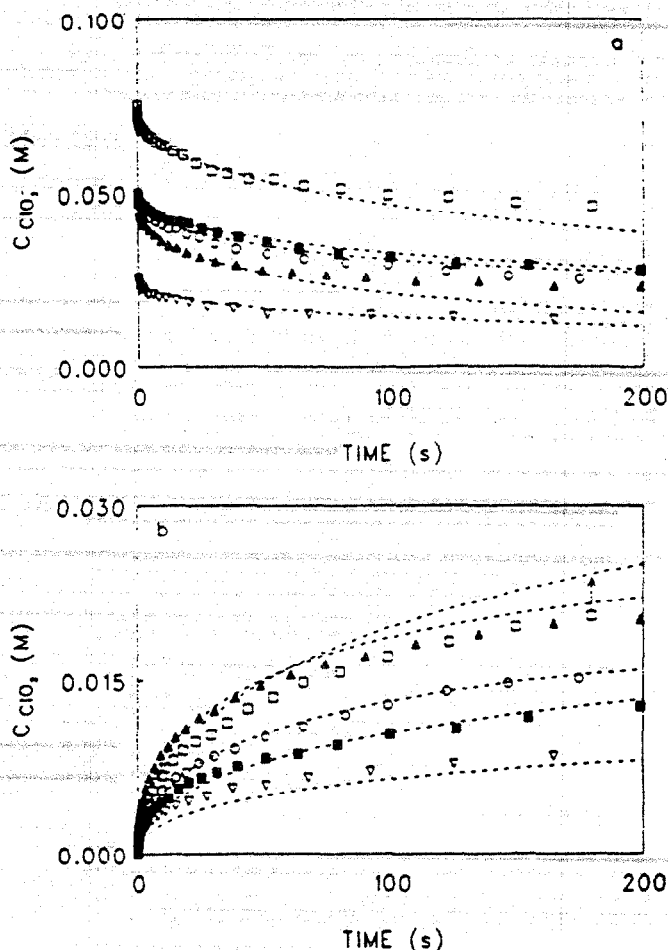


Figure 6. Comparison of a few experimental and simulated (dashed lines) kinetic curves for chlorite ion (a) and chlorine dioxide (b): $C_{\text{ClO}_2^-} = 4.99 \times 10^{-2} \text{ M}$, $C_{\text{Fe}^{2+}} = 1.39 \times 10^{-3} \text{ M}$, pH = 1.25 (\blacksquare); $C_{\text{ClO}_2^-} = 4.99 \times 10^{-2} \text{ M}$, $C_{\text{Fe}^{2+}} = 1.39 \times 10^{-3} \text{ M}$, pH = 2.00 (\circ); $C_{\text{ClO}_2^-} = 5.00 \times 10^{-2} \text{ M}$, $C_{\text{Fe}^{2+}} = 4.20 \times 10^{-3} \text{ M}$, pH = 1.75 (\blacktriangle); $C_{\text{ClO}_2^-} = 2.50 \times 10^{-2} \text{ M}$, $C_{\text{Fe}^{2+}} = 1.39 \times 10^{-3} \text{ M}$, pH = 1.75 (∇); $C_{\text{ClO}_2^-} = 7.50 \times 10^{-2} \text{ M}$, $C_{\text{Fe}^{2+}} = 1.39 \times 10^{-3} \text{ M}$, pH = 1.75 (\square).

curves. In the first attempt, all reaction steps were included in the calculations with the originally proposed rate constants (set A in Table IV). With this set of data, a consistently smaller than experimentally observed decomposition rate was calculated for the initial part of the reaction. Also, at longer times the chlorine dioxide production was overestimated and the stoichiometry was consistent with reaction 2. Sensitivity analysis of the parameters confirmed that the reactions between various transient species have, at most, marginal kinetic importance, even if they are assumed to be diffusion controlled. Therefore, reactions 17, and as a consequence 18, and 19 were rejected in further calculations.

The rate-determining step in the overall mechanism is the redox decomposition of the FeClO_2^{2+} complex. Thus, the calculated kinetic curves are very sensitive to the actual parameters for reaction 5. Simultaneously increasing k_6 and decreasing K_6 (i.e. increasing k_4) resulted in simulated concentration vs time profiles for the chlorite ion that approached the experimentally observed curves. The calculations, based on systematic variation of the parameters, gave 100 s^{-1} and $1.3 \times 10^{-3} \text{ M}$ as the best values for k_6 and K_6 , respectively. Modification of these parameters did not affect the stoichiometry of the reaction.

In contrast to chlorine dioxide, chlorate ion is formed only in fast secondary steps between various chlorine species. Thus, the only possible way to resolve the discrepancy between the measured and calculated stoichiometries is to modify the intrinsic rate constants for the ClO_2^- -HOCl reaction. This would require that the value for the k_{11}/k_{12} ratio be about 3 orders of magnitude smaller. The literature value for k_{11}/k_{12} ($5.4 \times 10^4 \text{ M}^{-1}$) was calculated¹¹ without rigorous confirmation of the stoichiometry by fitting the concentration vs time profiles for chlorite ion in the ClO_2^- -HOCl reaction. Simulated kinetic curves calculated

(30) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* 1962, 84, 1355.

(31) Roth, W. A. *Z. Phys. Chem., Abt. A* 1929, 145, 289.

(32) Cain, C. G.; Crist, D. R. *J. Am. Chem. Soc.* 1972, 94, 3195.

(33) Auel, G. C. *J. Chem. Soc.* 1950, 1286.

(34) Beach, M. W.; Margerum, D. W. *Inorg. Chem.* 1990, 29, 1225.

(35) Hindmarsh, A. C. *GEAR: Ordinary Differential Equation Solver*. Technical Report No. UCM-3001, Revision 2; Lawrence Livermore Laboratory: Livermore, CA, 1972.

(36) Peintler, G. Private communication. ZITA 2.1, a software package for simulating and fitting kinetic curves; Szeged, Hungary, 1991.

Table IV. Proposed Mechanism for the Iron(III)-Catalyzed Decomposition of Chlorite Ion

reaction	rate constant ^a		
	set A	ref ^b	set B ^c
Complex Formation			
$\text{H}^+ + \text{ClO}_2^- = \text{HClO}_2$ $K_1 = 52.5 \text{ M}^{-1}$	fast equil		
$\text{Fe}^{3+} = \text{Fe}(\text{OH})^{2+} + \text{H}^+$ $K_2 = 1.82 \times 10^{-3} \text{ M}$	fast equil		
$\text{Fe}^{3+} + \text{ClO}_2^- = \text{FeClO}_2^{2+}$ $K_3 = 13.8 \text{ M}^{-1}$	k_3 k_{-3}	10 10	2.7×10^2 19.5
$\text{Fe}(\text{OH})^{2+} + \text{ClO}_2^- = \text{Fe}(\text{OH})\text{ClO}_2^-$ $K_4 K_5 = 7.6 \times 10^3 \text{ M}^{-2}$	k_4 k_{-4}/K_5	10 10	5.0×10^3 0.66
$\text{Fe}(\text{OH})\text{ClO}_2^- + \text{H}^+ = \text{FeClO}_2^{2+}$ $K_4 K_5 = 7.6 \times 10^3 \text{ M}^{-2}$	fast equil		
Decomposition of the FeClO_2^{2+} Complex			
$\text{FeClO}_2^{2+} = \text{Fe}^{2+} + \text{ClO}_2$ $K_6 = 2.0 \times 10^{-5} \text{ M}$	k_6 k_{-6}	10 9	100 7.6×10^6
Oxidation of Fe^{2+}			
$\text{Fe}^{2+} + \text{ClO}_2^- \rightarrow \text{Fe}^{3+} + \text{Cl}(\text{II})$ $\text{Fe}^{2+} + \text{HClO}_2 \rightarrow \text{Fe}^{3+} + \text{Cl}(\text{II})$ $\text{ClO}_2^- + \text{Cl}(\text{II}) \rightarrow \text{HOCl} + \text{ClO}_2$	k_7 k_8	24 24	1.9×10^3 3.0×10^3
Reactions of Chlorine Species			
$\text{HOCl} + \text{HClO}_2 = \text{Cl}_2\text{O}_2 + \text{H}_2\text{O}$ $\text{Cl}_2\text{O}_2 + \text{ClO}_2^- = 2\text{ClO}_2 + \text{Cl}^-$ $\text{Cl}_2\text{O}_2 (+\text{H}_2\text{O}) = \text{ClO}_3^- + \text{Cl}^- + 2\text{H}^+$ $\text{HOCl} + \text{Cl}^- + \text{H}^+ = \text{Cl}_2 (+\text{H}_2\text{O})$ $K_{13} = 1.7 \times 10^3 \text{ M}^{-2}$ $\text{Cl}_2 + \text{ClO}_2^- = \text{Cl}_2\text{O}_2 + \text{Cl}^-$ $2\text{HOCl} = \text{Cl}_2\text{O} (+\text{H}_2\text{O})$ $K_{15} = 1.15 \times 10^{-2} \text{ M}^{-1}$ $2\text{HOCl} + \text{H}^+ = \text{Cl}_2\text{O} + \text{H}^+ (+\text{H}_2\text{O})$ $K_{16} = K_{15}$ $\text{Cl}_2\text{O} + \text{ClO}_2^- = \text{ClO}_3^- + \text{Cl}_2$ $\text{Cl}_2\text{O}_2 + \text{HOCl} = \text{ClO}_3^- + \text{Cl}_2 + \text{H}^+$	k_{10} k_{11}^d k_{12}^d k_{13} k_{-13} k_{14} k_{15} k_{-15} k_{16} k_{-16} k_{17} k_{18}	2.1×10^4 5.0×10^4 9.3×10^3 1.8×10^4 11 3.7×10^3 0.12 11 3.1 2.7×10^2 1.8×10^5 5.0×10^4	11 11 11 30 30 11 34 34 32 32 <i>e</i> <i>e</i>
			2.1×10^4 5.0×10^4 1.0×10^7 1.8×10^4 1.1×10 3.7×10^3

^a First-, second-, and third-order rate constants are in s^{-1} , $\text{M}^{-1} \text{s}^{-1}$, and $\text{M}^{-2} \text{s}^{-1}$, respectively. ^b The rate constants in set A were directly obtained from or estimated on the basis of the corresponding reference. ^c See text. ^d According to ref 11, $k_{11}/k_{12} = 5.4 \times 10^4 \text{ M}^{-1}$. ^e Estimated in this work.

on the basis of the modified set of rate constants (set B, Table IV) correlate excellently with the experimental results. Examples are shown in Figure 6.

At longer reaction times and at higher pH values and chlorite ion and iron(III) concentrations, the calculations tend to predict faster than observed decomposition. This finding strongly suggests that the inclusion of additional steps may be necessary to obtain a more precise mechanism for the decomposition.

Theoretically, a better data set could be obtained for the rate constants by combining the simulations with a nonlinear least-squares fitting procedure as is described in detail elsewhere.¹¹ However, a meaningful fitting procedure will require more reliable parameters for several independent steps of the mechanism, such as the rate constants of the $\text{HOCl}-\text{ClO}_2^-$ reaction and the equilibrium constant for reaction 5. Because of the lack of these data, which necessarily must be obtained from independent studies, no further attempt was made to optimize the kinetic model.

Conclusions. The application of a variety of fast kinetic techniques made it possible to explore the initial part of the iron(III)-catalyzed chlorite ion decomposition. It was demonstrated that the QSF method can successfully be used for studying inorganic reactions. The main advantage of this method over other fast kinetic techniques is that the samples can be analyzed by using conventional analytical procedures and the concentration vs time profiles are readily obtained for the reactants and products. The cumulative dead time is about 1 order of magnitude higher than it is with the SF method. However, this disadvantage is partly offset by the fact that the same rate constants can be determined by using lower initial reactant concentrations. This is because pseudo-first-order conditions do not have to be maintained during the kinetic runs.

In spite of the obvious advantages, the QSF method cannot substitute completely for other fast kinetic techniques because it is not suitable for the detection and identification of reactive transient species. Therefore, the QSF, SF, and SF-RS methods

should be considered as complementary techniques which together may provide comprehensive kinetic information for a wide variety of reactions.

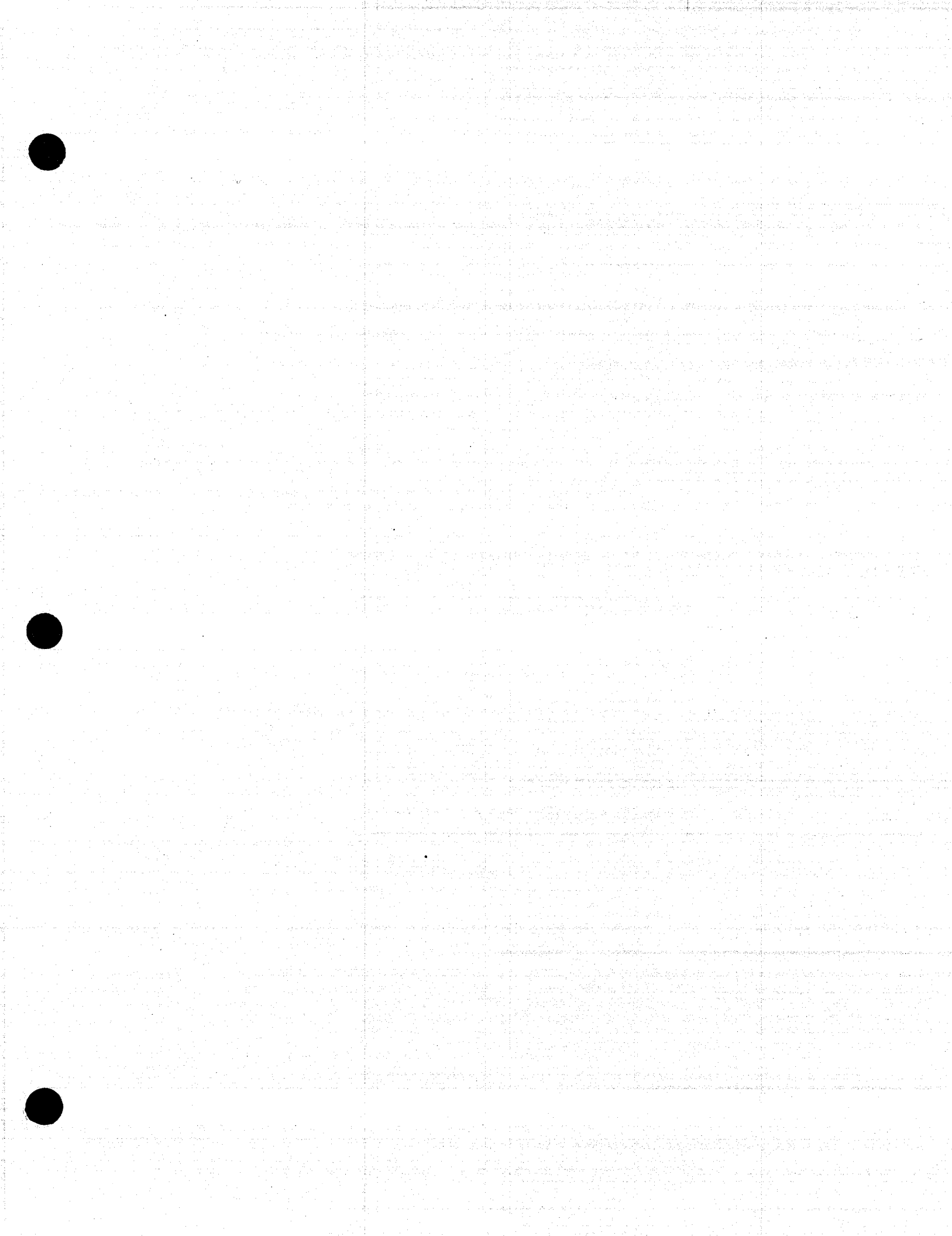
The kinetic model obtained for the decomposition of chlorite ion gives a reasonable description of the reaction rate and stoichiometry. It was confirmed that the precursor in this mechanism is the FeClO_2^{2+} complex and the rate-determining step is its redox decomposition. Although the calculations indicated that additional steps may have some effect on the reaction, we believe that a kinetically significant steps have been included in the mechanism for the conditions applied in this study. In other words, the mechanism proposed corresponds to the minimum basis set of reactions. However, it should be emphasized that if the experimental conditions are significantly different from those reported here, the mechanism may prove to be incomplete, requiring the postulation of other reaction steps.

On the basis of the mechanism, the possible effects of iron impurities on the reactions of chlorite ion can be estimated. For example, in the presence of 10^{-6} M iron(III) and at pH ~ 2.0 2–4% of the chlorite ion decomposes in about 5 min, after which the decomposition practically stops. In terms of stoichiometry this concentration change may be negligible, but the kinetic role of the transient species formed in the catalytic reaction may be significant. Also, in open reaction systems, which allow the loss of chlorine dioxide, the effects of the decomposition may be more pronounced. The results indicate that impurities may significantly alter the reactions of chlorite ion even at very low concentration levels.

001617

Acknowledgment. We thank Mr. Gábor Peintler of Szeged Hungary, for the actual version of the program ZITA used in the calculations. We also express our gratitude to Merrell Dow Chemicals (Cincinnati, OH) for lending us the quenched stopped-flow instrument.

Registry No. ClO_2^- , 14798-27-7; Fe, 7439-89-8.





Removing Chlorite by the Addition of Ferrous Iron

Angela Iatrou and William R. Knocke

The application of chlorine dioxide in water treatment has been limited because of concerns about the health effects of residual chlorite (ClO_2^-) and chlorate. This study investigated the feasibility of using ferrous iron (Fe(II)) to reduce chlorite concentrations. Laboratory tests indicated a required reaction stoichiometry of 3.0–3.1 mg $\text{Fe(II)}/\text{mg ClO}_2^-$. The reaction rate was rapid for pH values of 5 and greater. Interference from dissolved oxygen was minimal. The ferric hydroxide solids produced as a by-product of the $\text{Fe(II)}-\text{ClO}_2^-$ reaction had no adverse effect on alum coagulation for the removal of turbidity and dissolved organic carbon.

The use of chlorine dioxide (ClO_2) as an oxidant or disinfectant (or both) in drinking water treatment has frequently been considered by utilities seeking to control

trihalomethanes. However, one major problem is that 50–70 percent of the applied ClO_2 often remains as residual chlorite (ClO_2^-).¹ Concern about residual concentrations of ClO_2 , ClO_2^- , and chlorate (ClO_3^-) has resulted in limitations on the dosages of ClO_2 applied. Elimination of these reaction by-products by further re-

duction to Cl^- could greatly enhance the potential for ClO_2 usage in drinking water treatment.

Recent studies have investigated the use of granular activated carbon (GAC) and reduced sulfur compounds for possible elimination of ClO_2^- . Gordon et al.² published information regarding the stoichiometry and rate of reaction between sulfur dioxide-sulfite ion and ClO_2^- . These authors found that 90 percent of ClO_2^- could be removed with reaction times <15 min. However, Dixon and Lee³ reported that the reaction of sulfur dioxide with ClO_2^- led to the formation of significant amounts of ClO_3^- in waters containing dissolved oxygen (DO). GAC columns were shown to have limited effectiveness for ClO_2^- re-

full report of this project will be available from the AWWA Research Foundation, 6666 W. Quincy Ave., Denver, CO 80235.

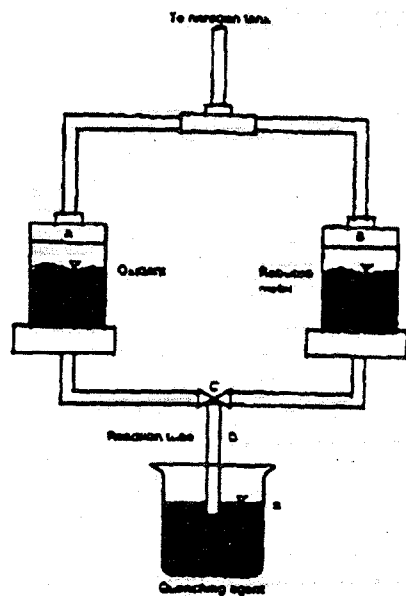


TABLE 1
Stoichiometry of reaction between ferrous iron and chlorite

Solution pH	ClO_2^- Dose mg/L	Residual ClO_2^- mg/L	Residual Fe(II) mg/L	Reaction Ratio mg $\text{Fe(II)}/\text{mg ClO}_2^-$
5.0*	1.1	<0.1	12.2	5.1
	4.4	<0.1	2.3	3.0
	8.8	3.9	<0.1	3.2
	13.2	8.2	<0.1	3.1
5.0†	1.2	<0.1	4.6	3.0
	2.4	0.1	1.2	3.0
	2.2	<0.1	8.4	2.3
	4.4	<0.1	2.0	3.1
6.0*	8.8	3.8	<0.1	3.1
	1.2	<0.1	4.5	3.1
	2.4	0.2	1.5	3.0
	4.5	1.6	<0.1	2.6
7.0*	6.8	4.0	0.1	3.2
	13.2	8.3	<0.1	3.2
	2.4	<0.1	0.2	3.3
	4.8	2.0	<0.1	2.9
				3.1‡

*Initial ferrous iron concentration—15.7 mg/L

†Initial ferrous iron concentration—8.2 mg/L

‡Average ratio

Figure 1. Schematic of experimental apparatus used for kinetic studies

001618

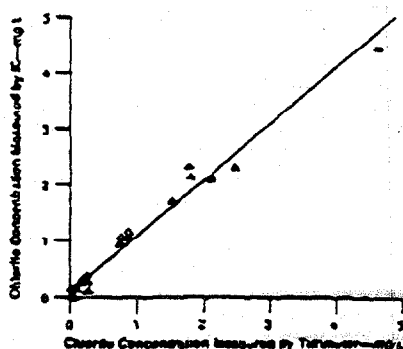


Figure 2. Comparing measurement of residual chlorite by a computer-aided titrimeter and by an ion chromatograph

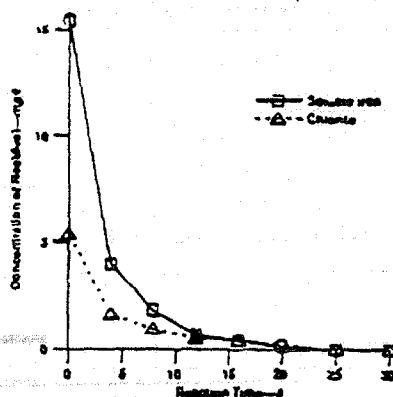


Figure 3. Reduction of chlorite by ferrous iron at pH 6 and initial ferrous iron to chlorite weight ratio of 3:1 (temperature—25°C)

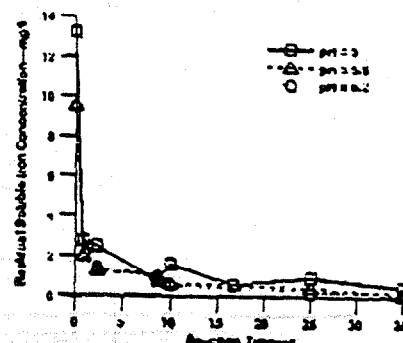


Figure 4. Effect of solution pH on the rate of reaction between ferrous iron and chlorite (temperature—25°C)

moval; some ClO_3^- formation was noted across the GAC medium. Griese et al.⁴ also found ClO_3^- formation to be a problem when using sulfur dioxide.

Ondrus and Gordon⁵ investigated the kinetics of interaction between ferrous iron (Fe(II)) and ClO_2^- , finding that acceptable rates of reaction could be achieved. These studies were conducted under conditions of extremely low pH and high ionic strength.

More recently, Griese et al.⁴ reported on laboratory- and pilot-scale studies at Evansville, Ind., in which Fe(II) effectively reduced ClO_2^- from drinking water. In this situation, no ClO_3^- appeared to be formed as a by-product of the ClO_2^- reduction reaction. It should be noted that excess Fe(II) dosages (well above the stoichiometric requirement) were utilized but the authors did not investigate the fate of the excess Fe(II) .

Another area of specific concern regarding ClO_2 usage is the presence of residual ClO_2^- . Chlorate is formed as a by-product of feed stock impurity, because of inefficiencies during ClO_2 generation or by chemical oxidation of residual ClO_2^- . This research study did not evaluate the possible removal of residual ClO_2^- by Fe(II) .

The objectives of the study were

- to evaluate both the stoichiometry of and the reaction kinetics between Fe(II) and ClO_2^- as a function of solution pH, temperature, dissolved organic carbon (DOC) concentration, and DO concentration;
- to assess the potential for formation of ClO_3^- as a by-product of the $\text{Fe(II)}-\text{ClO}_2^-$ reaction;
- to assess the fate of iron during treatment, including potential problems that may develop as a result of excess Fe(II) addition; and
- to evaluate the effect of ferric hydroxide solids (formed as a by-product of the

$\text{Fe(II)}-\text{ClO}_2^-$ reaction) on alum coagulation for turbidity and DOC removal.

Experimental methods and materials

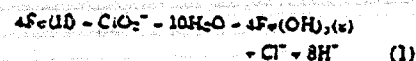
Test and stock solutions. All solutions were prepared using distilled, deionized water.* DO concentrations were minimized (<0.5 mg/L) by bubbling nitrogen gas through the solution for a minimum of 15 min prior to any chemical addition. Background ions added to the solution included sodium bicarbonate (1.5–2 meq/L), calcium chloride (1.0 meq/L), and sodium sulfate (0.25 meq/L) to simulate representative freshwater conditions. Solution pH was adjusted by the addition of either nitric acid or sodium bicarbonate and was monitored with a pH meter.[†]

Stock Fe(II) solutions were prepared using reagent-grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystals. Prior to Fe(II) addition, the solution was deaerated and acidified to pH 2.0 using nitric acid. Stock Fe(II) solutions were sealed with parafilm to minimize oxygen transfer and subsequent Fe(II) oxidation. Stock solutions were prepared at least every two days during testing or when any visual evidence of Fe(II) oxidation appeared in the stock solution.

The stock ClO_2^- solution was prepared by adding sodium chlorite (NaClO_2) flakes[‡] to distilled, deionized water. Solution pH was maintained >pH 7, thereby minimizing potential conversion of ClO_2^- to ClO_3^- .[§] The stock solution was sealed with parafilm and stored in an amber bottle in a cool, dark location. The titer of the stock was quantified daily using a computer-aided titrimeter.[§]

Sodium thiosulfate was used to quench all oxidation-reduction reactions. A stock solution was prepared using reagent grade $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. Thiosulfate may be slowly oxidized to sulfate by DO;⁷ therefore, fresh thiosulfate stock solutions were prepared weekly and sealed with parafilm.

Reaction stoichiometry and rates. The oxidation-reduction reaction between Fe(II) and ClO_2^- is



Calculations based on this molar stoichiometry predict that 3.3 mg Fe(II) are required to completely reduce 1.0 mg ClO_2^- . Several tests were conducted using initial Fe(II) concentrations near 8 and 16 mg/L, with ClO_2^- dosages ranging from approximately 50 to 300 percent of the theoretical amount required for Fe(II) oxidation. Tests were conducted at pH values of 5, 6, and 7. Samples were analyzed for residual soluble iron and ClO_2^- concentrations after a 5-min reaction period.

The kinetics of $\text{Fe(II)}-\text{ClO}_2^-$ interaction were quantified by use of a set of pressurized reaction chambers (schematic shown in Figure 1). A ClO_2^- solution was contained in vessel A, and an Fe(II) solution was placed in vessel B. The initial concentration of each chemical species was doubled so that the desired reactant concentrations were achieved once the solutions were mixed. Flow was initiated and ceased by the master valve at C. The reaction occurred in tube D and was quenched by allowing the solution to flow into a holding vessel (E) containing a 10× stoichiometric excess of sodium thiosulfate.

Reaction time was established by control of the system flow rate and the length of tube D. Applied cell pressure ranged from 6 to 20 psi; tube (0.096-cm-diameter) lengths ranged from 1.5 to 9.0 m. This combination produced reaction times between 0.6 and 36 s in tube D. Flow rates were maintained well above 0.2 m/s in the tube, thereby ensur-

*Milli-Q Millipore Corp., Milford, Mass.
†Model 230 Fisher Scientific Co., Pittsburgh, Pa.
‡EM Science, Cherry Hill, N.J.
§Model 450 Fisher-Porter, Warrington, Pa.

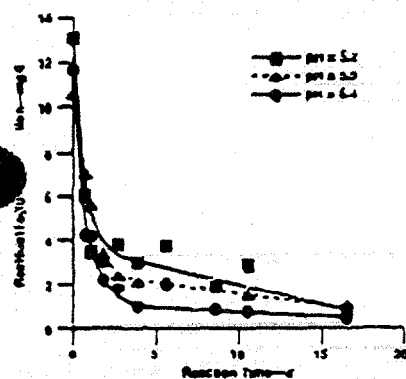


Figure 5. Effect of reduced solution temperature and of pH on the rate of reaction between ferrous iron and chlorite (temperature—5–6°C)

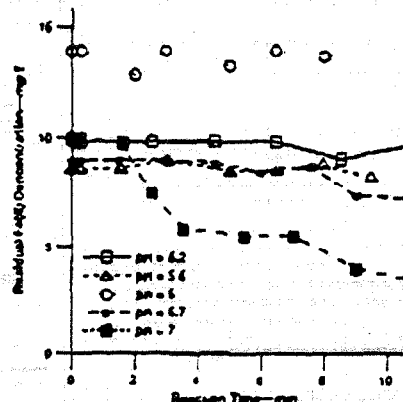


Figure 6. Effect of solution pH on the stability of ferrous iron in oxygenated waters (temperature—25°C, DOC <1 mg/L)

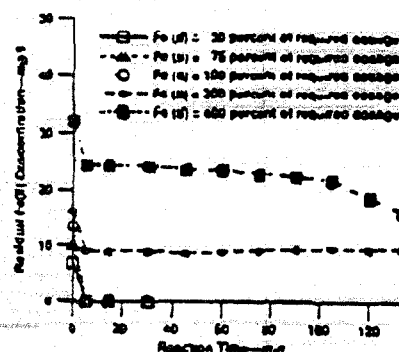


Figure 7. Effect of ferrous iron dosage and the presence of dissolved oxygen on residual iron concentration following reaction with chlorite at pH 5.5 (DOC <1 mg/L, temperature—25°C)

ing essentially instantaneous mixing at valve C.

Sodium thiosulfate was selected as the quenching agent based on preliminary studies that showed (1) the reaction between $S_2O_3^{2-}$ and ClO_2^- was much faster than the $Fe(II)-ClO_2^-$ interaction when a large excess of thiosulfate was present and (2) the presence of an excess of thiosulfate in solution did not promote reduction of $Fe(OH)_3(s)$ formed during the $Fe(II)-ClO_2^-$ reaction. The latter was important because the reaction rate was ultimately based on the disappearance of $Fe(II)$ from solution.

Rate studies were conducted over the pH range 5–6.5 using a solution temperature of 25°C. pH values <5 were not tested because they were considered unrealistic for conventional water treatment practice. Testing at pH >6.5 was not done because competitive $Fe(II)$ oxidation by traces of DO made interpretation of the data difficult. Selected studies were conducted at lower temperatures (5–6°C) by placing the pressure chambers, quenching vessel, and all system tubing in a constant-temperature bath.

Competitive reactions with DO. DO in water at treatment facilities might compete with ClO_2^- for the oxidation of $Fe(II)$, possibly resulting in excess residual ClO_2^- concentrations. Experiments were conducted to quantify the relative reaction rates of the $Fe(II)-ClO_2^-$ and $Fe(II)-DO$ reactions. One set of experiments involved adding $Fe(II)$ to solutions containing 9–10 mg DO/L and monitoring for $Fe(II)$ over time for up to 15 min. This experiment was conducted at five pH values between 5 and 7.

It was important to determine whether DO would efficiently remove any excess $Fe(II)$ that remained following the ClO_2^- reduction reaction. The fate of excess iron is important because most water treatment facilities desire an Fe concentra-

tion in finished water <0.3 mg/L. In these experiments, solutions containing approximately 4 mg ClO_2^- /L and 9–10 mg DO/L were dosed with $Fe(II)$ at levels ranging from 25 to 400 percent of the stoichiometric requirement for ClO_2^- reduction. Samples were withdrawn from each beaker every 10–15 min for up to 2 h and were analyzed for residual ClO_2^- and $Fe(II)$ concentrations. These tests were conducted at pH 5.5, 6.3, and 7.

Coagulation experiments. A standard six-piece jar-test apparatus* was used to evaluate the effect of iron (added for ClO_2^- reduction) on turbidity and DOC removal with alum as the primary coagulant. All coagulation experiments were conducted in the pH range 6.2–6.5. Solutions were prepared with the same background ion concentrations as previously described. In addition, approximately 100 mg/L of bentonite clay was added to yield an initial turbidity of 25–30 ntu.

The DOC source for the coagulation experiments was fulvic acids that were concentrated from the Dismal Swamp near Suffolk, Va. Aquatic DOC was separated from the swamp water using resin according to adsorption-separation methods described by Thurman and Malcolm.⁹

Coagulation experiments used a 100 percent stoichiometric $Fe(II)$ dosage for ClO_2^- reduction coupled with varying dosages of alum. Both chemicals were added simultaneously at the beginning of the high-speed (150 rpm) rapid-mix period (detention time = 90 s). Two-stage flocculation was simulated using 15 min of mixing at 50 rpm followed by 15 min at 20 rpm. Following a 1-h sedimentation period, samples were withdrawn and analyzed for residual turbidity and total iron concentration. A portion of each sample was filtered through a 0.2- μ m filter and analyzed for soluble iron, ClO_2^- , and DOC concentrations. Particulate iron concentration was calculated and

was reported as the difference between total and soluble iron concentrations.

Analytical procedures. Solution ClO_2^- concentration was analyzed using a programmable titrator according to methods described by Ajeta et al.⁷ Samples were initially reacted with potassium iodide followed by titration with a standardized phenylarsine oxide solution. Approximately 50 samples were also analyzed for residual ClO_2^- by ion chromatography, with results showing excellent agreement between the two methods (Figure 2).

Residual ClO_2^- concentration could not be measured directly in kinetic experiments that utilized the pressure chamber apparatus because of the presence of sodium thiosulfate in the quenching vessel. For these experiments, residual ClO_2^- concentration was calculated based on the initial ClO_2^- concentration measured, the observed loss of iron during the reaction, and the observed stoichiometry of reaction between $Fe(II)$ and ClO_2^- .

Selected samples were analyzed for residual ClO_2^- concentration by use of an ion chromatograph. The eluent used was composed of 2.8 mM bicarbonate and 0.4 mM carbonate.

Initial and residual iron concentrations were analyzed according to either of the following methods. Most samples were filtered through a 0.2- μ m filter, acidified with nitric acid, and analyzed using an atomic absorption spectrophotometer.[†] Selected samples were also analyzed for $Fe(II)$ concentration using the bathophenanthroline procedure described by Lee and Stumm.¹⁰

Analysis of samples for residual DOC concentration involved filtration through a 0.2- μ m filter followed by the use of a total organic carbon analyzer ‡

*Model J200, Rhyne & Bird, Richmond, Va.
†Model 705, Perkin-Elmer, Norwalk, Conn.
‡DC-80, DuPont, Santa Clara, Calif.

turbidimeter.*

Results and discussion

Stoichiometry of $\text{Fe(II)}-\text{ClO}_2^-$ reaction. Results of several tests aimed at evaluating the reaction stoichiometry between Fe(II) and ClO_2^- are shown in Table 1. Although a range of values was observed, the average stoichiometry for all experiments was approximately 3.1 mg Fe/mg ClO_2^- . This value is slightly less than the theoretical reaction stoichiometry of 3.3 mg Fe/mg ClO_2^- calculated based on Eq 1. These results suggest that the predominant if not exclusive by-product of the ClO_2^- reduction reaction is chloride ion (Cl^-).

Kinetics of $\text{Fe(II)}-\text{ClO}_2^-$ reaction. Numerous experiments were conducted between pH 5 and 6.5 for assessing the rate of reaction between these two species. Typical results are shown in Figures 3-5. In these studies, an Fe(II) to ClO_2^- weight ratio of 3:1 was utilized. Data presented in Figure 3 show a rapid reduction of ClO_2^- within approximately 20 s at pH 6, even when starting with an initial ClO_2^- concentration >5 mg/L. Likewise, data shown in Figure 4 indicate a rapid reaction for three tests conducted over the pH 5-6.2 range. In this instance, decrease in solution iron concentration is graphed as an indicator of ClO_2^- reduction.

Data presented in Figures 3 and 4 relate to a solution temperature of 25°C. A slight decrease in reaction rate was observed when solution temperature decreased to 5-6°C (Figure 5). However, Fe(II) (and thus ClO_2^-) was still reacting at a rapid rate, as evidenced by the high percentage of iron that was oxidized within the first 10 s. These data indicate that the reduction of ClO_2^- by Fe(II) will easily occur within 1-2 min under the temperature conditions typically encountered in drinking water treatment.

Chlorate formation. A select number of experiments were undertaken in which solutions were monitored for the possible formation of ClO_3^- during the $\text{Fe(II)}-\text{ClO}_2^-$ reaction. Results shown in Table 2 indicate that no detectable amount of ClO_3^- was formed in solutions tested over the pH 5.5-8 range with initial ClO_2^- concentrations as high as 4.0 mg/L.

Effects of DO. Most studies were conducted with solutions that were deaerated by nitrogen during preparation to minimize the potential for Fe(II) oxidation by DO. Two groups of studies were conducted to assess the effect of DO on the $\text{Fe(II)}-\text{ClO}_2^-$ reaction. In the first set of studies, solutions containing Fe(II) were exposed to DO over the pH range 5.2-7; no ClO_2^- was present in these solutions. Results presented in Figure 6 indicate that Fe(II) was relatively stable in these solutions over approximately 10 min. Iron oxidation and precipitation were only signifi-

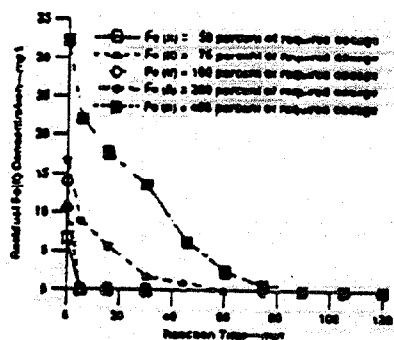


Figure 8. Effect of ferrous iron dosage and the presence of dissolved oxygen on residual iron concentration following reaction with chlorite at pH 6.3 ($\text{DOC} < 1 \text{ mg/L}$; temperature—25°C)

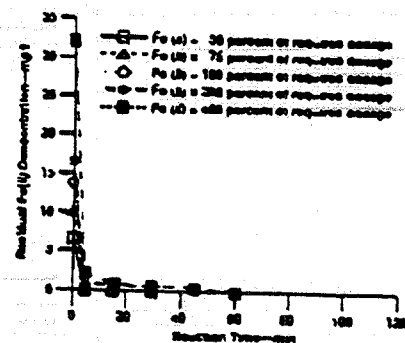


Figure 9. Effect of ferrous iron dosage and the presence of dissolved oxygen on residual iron concentration following reaction with chlorite at pH 7 ($\text{DOC} < 1 \text{ mg/L}$; temperature—25°C)

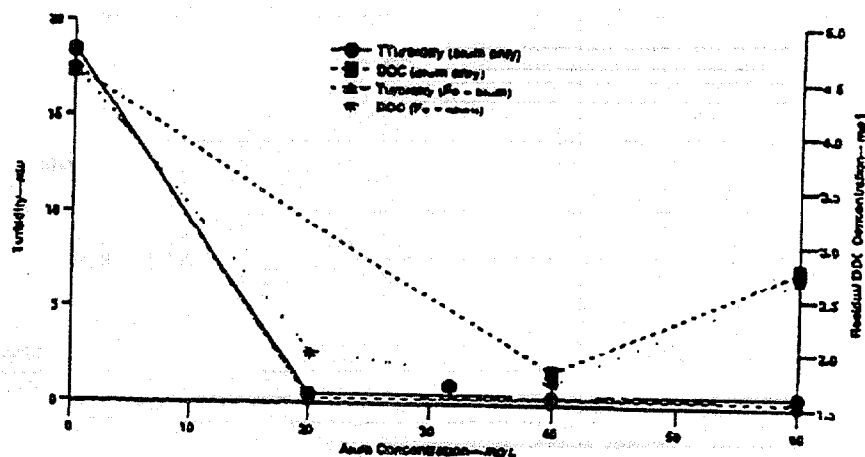


Figure 11. Removal of turbidity and DOC from water containing fulvic acid by alum coagulation alone and by ferrous iron plus alum coagulation ($\text{pH} = 6.3-6.5$, temperature—25°C)

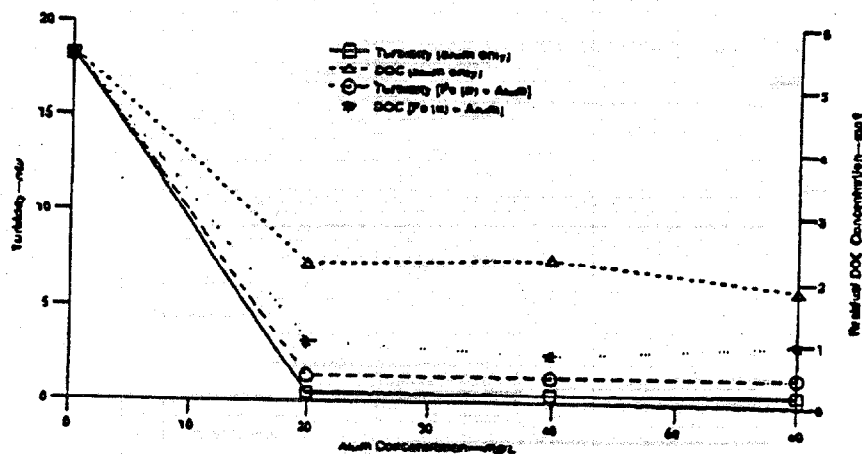


Figure 13. Removal of turbidity and DOC from water containing fulvic acid by alum coagulation alone and by ferrous iron plus alum coagulation ($\text{pH} = 6-3$, temperature—25°C)

*Model 2100 Neph Co Loveland Co

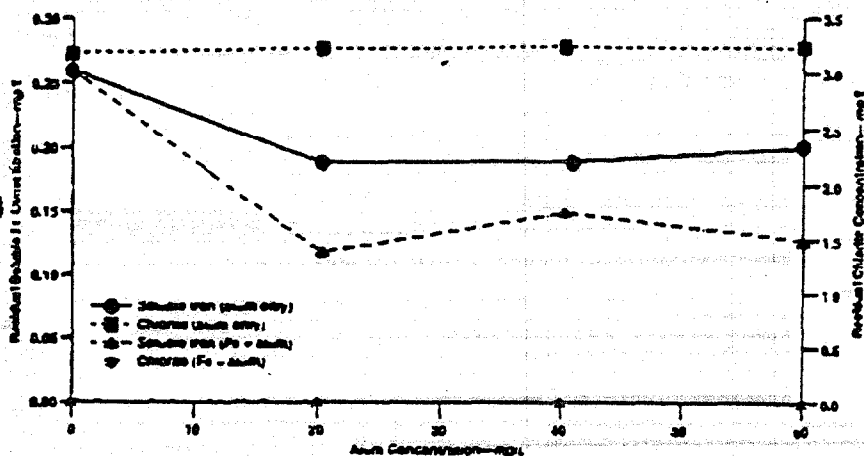


Figure 10. Residual soluble iron and chlorite concentrations following treatment of water containing fulvic acid by alum coagulation alone and by ferrous iron plus alum coagulation (pH—6.3–6.5; temperature—25°C)

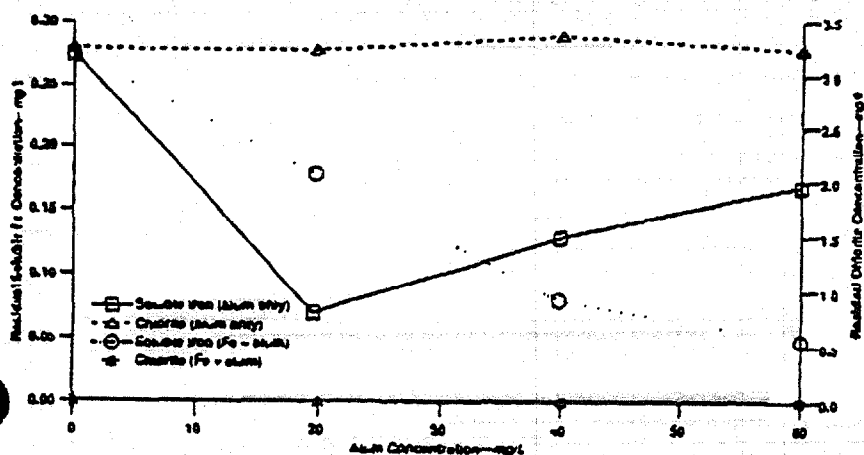


Figure 12. Residual soluble iron and chlorite concentrations following treatment of water containing fulvic acid by alum coagulation alone and by ferrous iron plus alum coagulation (pH—6.3; temperature—25°C)

TABLE 2
Chlorate formed as a by-product of the Fe(II)–ClO₂[−] reaction

Solution pH	Fe(II) Dose percent stoichiometric	Residual ClO ₂ [−] and ClO ₃ [−] —mg/L			
		Initial ClO ₂ [−] = 2 mg/L		Initial ClO ₂ [−] = 4 mg/L	
		ClO ₂ [−] mg/L	ΔClO ₃ [−] mg/L	ClO ₂ [−] mg/L	ΔClO ₃ [−] mg/L
5.5	50	0.77	<0.03	1.8	<0.03
	100	<0.03	<0.03	0.24	<0.03
	150	<0.03	<0.03	0.12	<0.03
6.5	50	0.88	<0.03	1.54	<0.03
	100	0.06	<0.03	0.32	<0.03
	150	<0.03	<0.03	0.09	<0.03
8.0	50	0.90	<0.03	2.47	<0.03
	100	0.17	<0.03	0.28	<0.03
	150	0.03	<0.03	0.09	<0.03

^aIndicates the increase in ClO₃[−] that takes place during ClO₂[−] reduction

indicate that over the pH range of this study, the competitive effect of DO on the reaction between Fe(II) and ClO₂[−] was minimal. This would mean that stoichiometric doses of Fe(II) should be sufficient to remove ClO₂[−] from waters containing significant DO concentrations.

Other studies were conducted in which DO and ClO₂[−] were both present in solution at the time the Fe(II) was added. DO concentrations in these studies were typically in the range of 9–10 mg/L, whereas Fe(II) dosages varied from 50 to 400 percent of the stoichiometric requirement for ClO₂[−] reduction. Results (Figures 7–9) show that Fe(II) reacted rapidly with the ClO₂[−], as evidenced by the initial steep decline in soluble iron concentration. Analysis of each solution indicated essentially 100 percent ClO₂[−] removal at Fe(II) dosages of 100 percent and higher on a stoichiometric basis.

The behavior of the excess iron in solution as a function of solution pH was interesting. Waters near pH 5.5 (Figure 7) showed minimal removal of excess Fe(II) over time, indicating little interaction of the Fe(II) with the DO present. When the solution pH was increased to 6.3 (Figure 8), excess Fe(II) was eliminated over a period of approximately 1 h, presumably because of oxidation by DO followed by Fe(OH)₃(s) precipitation. Only at pH 7 (Figure 9) was the excess Fe(II) rapidly eliminated via reaction with DO. These results correspond well to the results of Stumm and Lee¹¹ who showed that the kinetics of Fe(II) oxidation by DO were slow for pH values <6.5.

The practical application of these results relates to the fate of Fe(II) that is added in excess of the requirement for ClO₂[−] reduction. Surface waters that are treated at pH values in the neutral or alkaline range would probably not experience problems associated with high residual iron concentrations resulting from Fe(II) oxidation by DO. However, excess dosages of Fe(II) may persist under acidic treatment conditions and require some form of alternate oxidation, e.g., chlorine addition, to reduce the residual iron to levels below the recommended drinking water concentration of 0.3 mg/L.

Coagulation studies. Coagulation studies were conducted with fulvic acid-laden water samples in which a 100 percent Fe(II) dosage (stoichiometric for ClO₂[−] reduction) was coupled with various alum dosages in the pH 6.3–6.5 range. Companion coagulation studies were conducted in which no Fe(II) was added. Results from two separate pairs of coagulation studies (Figures 10–13) indicate that alum addition alone (no Fe(II) added) did not result in ClO₂[−] removal. In comparison, residual ClO₂[−] levels were <0.05 mg/L for all samples that received the 100 percent stoichiometric dose of Fe(II) (Figures 10 and 12). Further, the addition of Fe(II) did not hin-

TABLE 3
*Effect of point of addition of ferrous iron on alum coagulation of DOC-laden water**

Treatment Provided	Residual Turbidity ntu	Concentration of Residual—mg/L		
		ClO ₂ ⁻	DOC	Soluble Fe
No treatment (control)	27	3.3	6.2	0.16
Alum only: no Fe(II) added				
Alum dose = 20 mg/L	20	3.1	5.9	0.16
Alum dose = 60 mg/L	17	3.1	3.2	0.04
Fe(II) added prior to alum during rapid mix				
Alum dose = 20 mg/L	1.3	<0.05	3.0	0.09
Alum dose = 60 mg/L	1.5	<0.05	4.6	
Fe(II) and alum added simultaneously during rapid mix				
Alum dose = 20 mg/L	2.0	<0.05	2.6	0.21
Alum dose = 60 mg/L	1.2	<0.05	2.2	0.22
Fe(II) added during flocculation, alum added during rapid mix				
Alum dose = 20 mg/L	1.0	<0.05	2.3	0.28
Alum dose = 60 mg/L	1.3	<0.05	2.2	0.17

*In all studies, Fe(II) dose = 10 mg/L, pH = 6.3–6.5

der the performance of alum with respect to turbidity or DOC removal; in fact, DOC removal was slightly enhanced by adding Fe(II) as well as alum (Figures 11 and 13). Finally, when a 100 percent stoichiometric dosage of Fe(II) was utilized, the residual iron concentrations after coagulation were all at or below the 0.3 mg/L level.

These coagulation studies involved the simultaneous addition of Fe(II) and alum during the rapid-mix phase. One set of coagulation tests was undertaken to assess how treatment performance was affected by varying the point of Fe(II) addition. Samples of water containing fulvic acid (DOC = 6.2 mg/L) and ClO₂⁻ (3.3 mg/L) were treated with a 100 percent stoichiometric Fe(II) dosage and either 20 or 60 mg alum/L. The Fe(II) dosage was added (1) 1 min prior to alum addition, (2) simultaneously with the alum, or (3) at the beginning of the flocculation period. Results shown in Table 3 indicate that at least for treatment of this fulvic acid-laden water source, the addition of Fe(II) before, along with, or shortly after the addition of alum did not significantly affect water treatment with respect to turbidity, DOC, residual ClO₂⁻, or iron concentration.

Although these results indicate that Fe(II) may be added at multiple application points in a water treatment facility, it is strongly recommended that similar testing be done at all facilities to ascertain the effect of the Fe(II)-ClO₂⁻ reaction on overall performance. For example, certain facilities may wish to add Fe(II) in the later stages of flocculation or to the filter-applied water. Such scenarios must be investigated to ensure that treatment operations will be efficient in capturing the resulting Fe(OH)₃(s) solids.

Conclusions

The primary objective of this study was to determine the feasibility of using Fe(II) for elimination of ClO₂⁻ from drinking

water. Secondary emphasis was placed on examining the effect of Fe(OH)₃(s) solids (formed as a by-product of the Fe(II)-ClO₂⁻ reaction) on the use of alum as a primary coagulant for turbidity and DOC removal.

Based on the data collected during the study, the following conclusions were formulated:

- The Fe(II)-ClO₂⁻ reaction is kinetically rapid over pH 5–7, with essentially complete ClO₂⁻ reduction occurring in reaction times as short as 5–15 s.

- Fe(II) doses of 3.0–3.1 mg Fe/mg ClO₂⁻ were found to effectively promote ClO₂⁻ reduction while also producing minimal residual soluble iron. This stoichiometry reasonably predicts Cl⁻ as the by-product of ClO₂⁻ reduction by Fe(II).

- Excess dosages of Fe(II) could be removed by reaction with DO under neutral pH conditions. However, stability of soluble iron may be a problem with excess Fe(II) dosages under acidic pH conditions. Oxygen was ineffective for Fe(II) oxidation for pH values <6.3.

- There was no evidence of ClO₃⁻ forming as a by-product of the Fe(II)-ClO₂⁻ reaction, suggesting that ClO₃⁻ formation should not be a problem in treatment facilities that utilize Fe(II) for ClO₂⁻ removal.

- The presence of Fe(OH)₃(s) formed as a by-product of the Fe(II)-ClO₂⁻ reaction did not adversely affect the performance of alum as a primary coagulant for turbidity and DOC removal.

Acknowledgment

This research was supported in part by the AWWA Research Foundation (AWWARF Contract 633-90). The assistance of Dan Dorlack, AWWARF project officer, is greatly appreciated. Because this article was not reviewed by AWWARF, the content and conclusions are the opinions of the authors and do not necessarily reflect the views of the founda-

cial products does not constitute endorsement or recommendation for use. Parts of this article were presented at the AWWA Annual Conference, Philadelphia, Pa., June 1991.

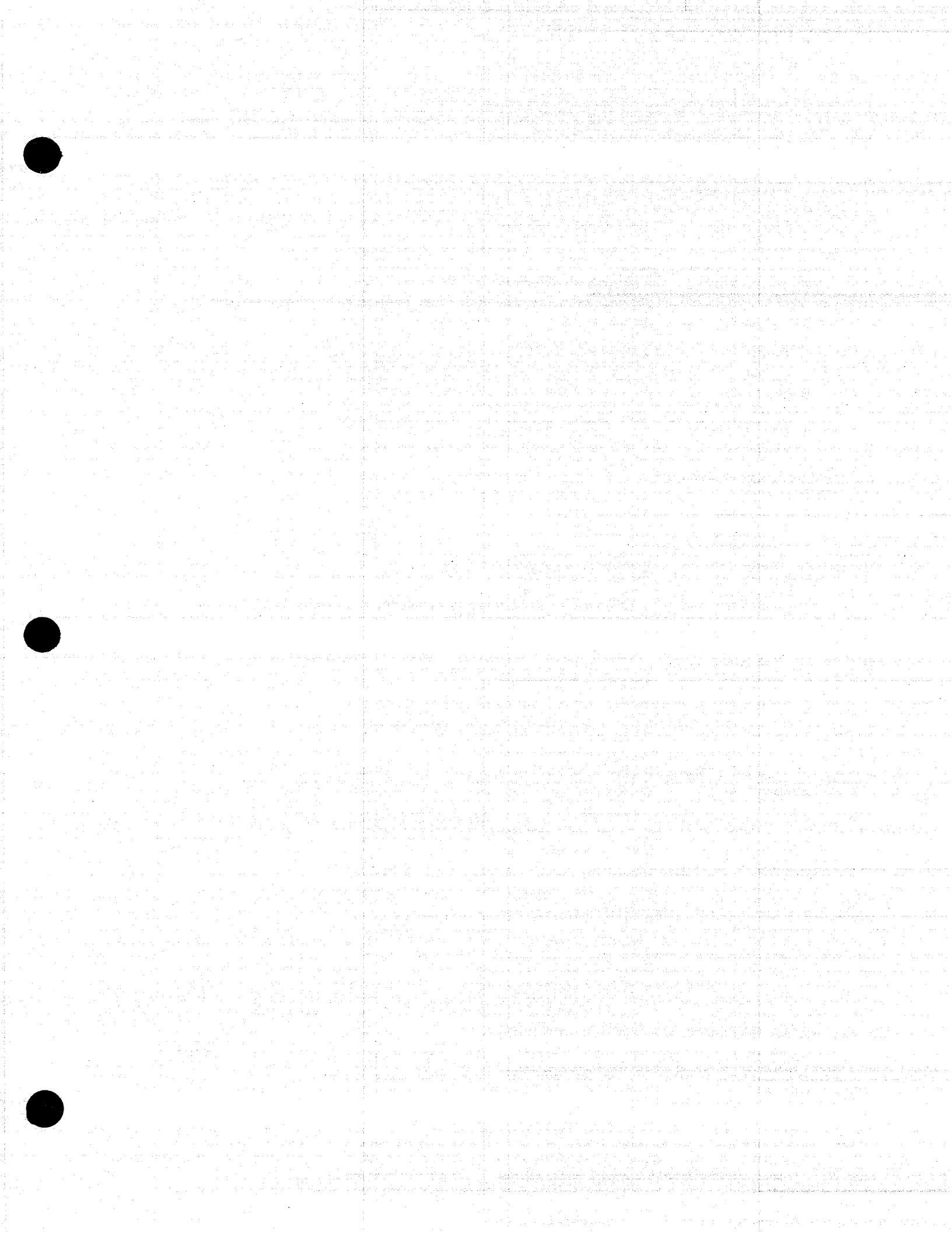
References

1. WERDEHOFF, K.S. & SINGER, P. C. Chlorine Dioxide Effects on THMFP TOXICITY and the Formation of Inorganic By-Products. *Jour. AWWA*, 79:9.107 (September 1987).
2. GORDON, G. ET AL. Minimizing Chlorite Ion and Chlorate Ion in Water Treated With Chlorine Dioxide. *Jour. AWWA*, 82:4.1 (Apr 1990).
3. DIXON, K.L. & LEE, R. C. The Effect of Sulfur-Based Reducing Agents and Carbon Filtration on Chlorine Dioxide By-Products. *Jour. AWWA*, 83:5.56 (May 1991).
4. GRIESE, M. H. ET AL. Using Reducing Agents to Eliminate Chlorine Dioxide and Chlorite Ion Residuals in Drinking Water. *Jour. AWWA*, 83:5.62 (May 1991).
5. ONDRUS, M.G. & GORDON, G. The Oxidation of Hexaquoiron(II) by Chlorine(II) in Aqueous Solution. *Inorg. Chem.*, 11:5.965 (1972).
6. GORDON, G., KIEFFER, R.G., & ROSENBLAT, D. H. The Chemistry of Chlorine Dioxide. *Progress in Inorganic Chemistry*, Vol. 1. John Wiley & Sons, New York (1972).
7. KULTHOFF, I. M. & SANDELL, E. B. *Textbook of Quantitative Inorganic Analysis*. The MacMillan Company, New York (3rd ed., 1956).
8. THURMAN, E.M. & MALCOLM, R.L. Preparative Isolation of Aquatic Humic Substances. *Envir. Sci. & Technol.*, 15:4.40 (1981).
9. AIETA, E.M.; ROBERTS, P.V.; & HERNANDEZ, M. Determination of Chlorine Dioxide, Chlorine, Chlorite, and Chlorate in Water. *Jour. AWWA*, 76:1.64 (Jan. 1984).
10. LEE, G.F. & STUMM, W. Determination of Ferrous Iron in the Presence of Ferric Iron Using Bathophenanthroline. *Jour. AWWA*, 52:12.1567 (Dec. 1960).
11. STUMM, W. & LEE, G.F. Oxygenation of Ferrous Iron. *Indus. Engrg. Chem.*, 53:2.143 (1961).



About the author:
Angela Iatrou is currently an associate engineer with James M. Montgomery Consulting Engineers, 3501 N. Causeway Blvd., Suite 300, Metairie, LA 70002. At the time

the work described in this article, she was a graduate student in the Department of Civil Engineering, Virginia Polytechnic Institute & State University (VPI), Blacksburg. Iatrou holds bachelor's degrees from Worcester Polytechnic Institute, Worcester, Mass., and Regis College, Weston, Mass., and an MS in environmental engineering from VPI. She is a member of AWWA and ASCE. William R. Knoche is professor of civil engineering, Department of Civil Engineering, 200 Patton Hall, VPI, Blacksburg, VA 24061.





BEST AVAILABLE COPY

Radiation Chemistry and Photochemistry of Oxychlorine Ions

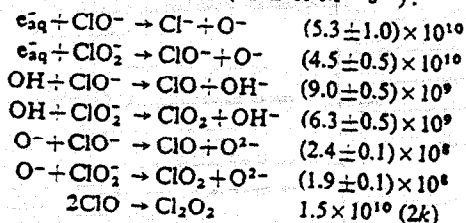
Part I.—Radiolysis of Aqueous Solutions of Hypochlorite and Chlorite Ions

BY G. V. BUXTON AND M. S. SUBHANI

Cookridge High Energy Radiation Research Centre,
Cookridge Hospital, Leeds LS16 6QB

Received 18th October, 1971

The radiolysis of aqueous solutions of ClO^- and ClO_2^- has been investigated using pulse and steady state methods. The absorption spectrum of ClO^- has been identified ($\lambda_{\text{max}} = 280 \text{ nm}$) and the complete reaction mechanism has been established in the case of ClO^- and proposed in the case of ClO_2^- . The following rate constants have been evaluated (units of $\text{M}^{-1} \text{s}^{-1}$):



Values of the radical and molecular yields obtained for dilute alkaline solution are:

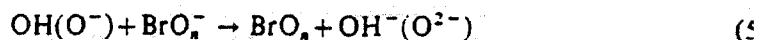
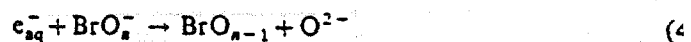
$$G(e_{\text{aq}}^-) + G(\text{H}) = 2.92 \pm 0.05, G(\text{OH}) = 2.41 \pm 0.12, \\ G(\text{H}_2) = 0.42 \pm 0.02 \text{ and } G(\text{H}_2\text{O}_2) = 0.70 \pm 0.01.$$

The photochemistry of oxyanions in aqueous solution is of considerable interest because of the number of different primary processes which these ions can undergo.¹⁻⁴ In many cases the commonest processes are those in which the oxidation number of the central atom changes by one unit through the formation of a hydrated electron, or a hydroxyl radical (processes (1) and (2)), or by two units through the formation of an oxygen atom (process (3)).



Quantitative determination of these processes for a given ion provides important information on the chemistry of its excited states, and also on the conditions under which particular radical species can be generated and their chemistry investigated. In the former case the quantities of interest are the quantum yields of the primary species and their dependence on the wavelength of the exciting light. In principle the quantum yields can be determined either by direct measurement of the yields of the primary products using flash photolysis, or by measuring the yields of the final products, establishing the mechanism of their formation and then deriving the yields of the primary species. In practice monochromatic light flashes of sufficient intensity are not yet available to make the first method useful quantitatively, but nevertheless flash photolysis is invaluable in determining the quality of the primary processes.

Quantitative information must therefore be obtained by the second method which requires that one knows the chemistry of the primary species and any other precursor of the final products. Much of this knowledge can be gained independently of the photochemical system from a study of the aqueous radiation chemistry of the particular ion where the reactions of e_{aq}^- and $\text{O}^-(\text{OH})$ with XO_n^- can be established beyond doubt. For example, in the case where $\text{X} = \text{Br}$, reaction (4)⁵ occurs for $n = 2$ and 3 and reaction (5) occurs for $n = 1$ and 2, and information was obtained on the absorption spectra and chemistry of BrO and BrO_2 which was essential to the interpretation of the photochemistry of BrO_n^- .⁶



We have adopted a similar approach in the case of oxychlorine ions whereby we have studied their aqueous radiation chemistry in order to obtain information which is essential to the elucidation of their aqueous photochemistry.

The steady state radiolysis of hypochlorite ion⁷ and chlorite ion⁸ solutions have been reported previously but the reaction mechanisms have not been established unequivocally, partly because the chemistry of the postulated intermediates ClO and Cl_2O_2 was not known with any certainty. In this paper we present the result of further investigation of the radiolysis of solutions of both these ions, using pulse and steady state methods, which provide detailed information on the chemistry of ClO and Cl_2O_2 . In each case a complete reaction mechanism has been established. The results also reveal a number of differences in the chemistry of the chlorine and bromine analogues.

EXPERIMENTAL

MATERIALS

All solutions to be irradiated were prepared from triply distilled water, and their pH was adjusted with sodium hydroxide.

Sodium hypochlorite solution was prepared by the method of Taylor and Bostock⁹ by distilling a mixture of 35 g of boric acid and 20 g of bleaching powder in 600 ml of water. The first 100 ml of distillate was collected in 400 ml of 2×10^{-2} M NaOH to give approximately 10^{-2} M ClO^- solution at pH ~ 12. Sodium chlorite (Hopkin and Williams technical grade) and sodium formate (B.D.H., reagent grade) were recrystallized three times from water. All other reagents were A.R. grade (B.D.H.) and were used without further purification.

Argon (99.995 %), nitrogen (white spot), oxygen (B.O.C.), and sulphur hexafluoride (Matheson) were taken straight from the cylinder. Nitrous oxide (B.O.C., anaesthetic grade) was passed through a column of potassium hydroxide pellets and then through a trap at -80° to remove any CO_2 or NO .

APPARATUS AND PROCEDURE

Details of sample preparation, apparatus and experimental procedure for γ -radiolysis and pulse radiolysis have been described elsewhere.¹⁰⁻¹¹

ANALYSIS

Nitrogen, hydrogen and oxygen were measured by gas chromatography using a column of molecular sieve 5A with argon as the carrier gas. The solution products ClO^- , ClO_2^- and ClO_3^- were determined by the following methods.

BEST AVAILABLE COPY

001625

ClO^-

This ion was determined either titrimetrically using arsenious oxide and iodine,¹² or spectrophotometrically at 292 nm taking $\epsilon_{\text{ClO}^-}^{292} = 419 \pm 10 \text{ M}^{-1} \text{ cm}^{-1}$ which we have determined and which agrees well with the value reported by Julien and Pucheault.⁷

 ClO_2^-

An aliquot of ClO_2^- solution was added to sufficient potassium iodide solution, adjusted to pH 2 with sulphuric acid, such that the final $[\text{I}^-] = 10^{-1} \text{ M}$. Under these conditions ClO_2^- oxidizes I^- to I_3^- quantitatively. I_3^- was measured spectrophotometrically at 350 nm.¹³

 $\text{ClO}^- + \text{ClO}_2^-$

To an aliquot of the mixture 5 to 10 drops of 5 % phenol solution were added to destroy ClO^- . The solution was allowed to stand for 10 min and then analyzed for ClO_2^- . The amount of ClO^- present in the mixture was then obtained spectrophotometrically by subtracting the known contribution of ClO_2^- ($\epsilon_{\text{ClO}_2^-}^{292} = 80 \text{ M}^{-1} \text{ cm}^{-1}$) from the total absorption measured at 292 nm.

 ClO_3^-

Chlorate ion usually had to be determined in the presence of ClO^- and ClO_2^- . This was achieved by measuring the sum of all three ions, using the method of Csanyi and Szabo,¹⁴ and subtracting the amounts of ClO^- and ClO_2^- determined as above. Chlorate ion does not interfere in these methods.

 ClO_2

Iodine dioxide was determined spectrophotometrically taking $\epsilon_{\text{ClO}_2}^{360} = 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Present it was removed by a stream of nitrogen before the other products were determined.

RESULTS

PULSE RADIOLYSIS

RATES OF REACTION OF e_{aq}^- , OH AND O^- WITH OXYCHLORINE ANIONS

Rate constants for the reactions of e_{aq}^- were obtained by direct observation of its decay at 575 nm. The presence of 10^{-5} M ClO^- or ClO_2^- enhanced the rate of decay of e_{aq}^- , but 10^{-1} M ClO_3^- had no effect, indicating that the first two ions react efficiently whereas ClO_3^- reacts very slowly if at all. Rate constants for the reactions

TABLE 1.—RATE CONSTANTS FOR THE REACTIONS OF e_{aq}^- , OH AND O^- WITH SOME OXYCHLORINE IONS

X	$k(e_{\text{aq}}^- + \text{X})/\text{M}^{-1} \text{ s}^{-1}$	$k(\text{OH} + \text{X})/\text{M}^{-1} \text{ s}^{-1}$	$k(\text{O}^- + \text{X})/\text{M}^{-1} \text{ s}^{-1}$
ClO^-	$(5.3 \pm 1.0) \times 10^{10}$	$(9.0 \pm 0.5) \times 10^9$	$(2.4 \pm 0.1) \times 10^8$
ClO_2^-	$(4.5 \pm 0.5) \times 10^{10}$	$(6.3 \pm 0.5) \times 10^9$	$(1.9 \pm 0.1) \times 10^8$
ClO_3^-	$< 10^6$	$< 10^6$	$< 10^6$

of OH and O^- were determined by the carbonate competition method¹⁵ by measuring the effect of $[\text{ClO}_3^-]$ on the yield of $\text{CO}_3^{\cdot -}$ produced on pulsing N_2O saturated solutions of 10^{-2} M CO_3^{2-} at pH 11 and 10^{-1} M CO_3^{2-} at pH 13 respectively. 10^{-1} M ClO_3^- had virtually no effect on the yield of $\text{CO}_3^{\cdot -}$ indicating that the hydroxyl radical also reacts inefficiently with this ion. The rate constant data are summarized in table 1.

ABSORPTION SPECTRUM OF ClO

On pulse radiolysis of N_2O or Ar saturated solutions of 10^{-3} M ClO^- at pH 11.4 transient species which absorbed between 250 nm and 350 nm was observed immediately after the pulse. Since ClO^- absorbs light in this region a correction for

001626

the removal of ClO^- during the pulse had to be made. This correction, expressed the change in optical density (ΔD_{ClO^-}), was calculated at each wavelength (λ) using eqn (6)

$$\Delta D_{\text{ClO}^-} = [G(-\text{ClO}^-)\epsilon_{\text{ClO}^-}^\lambda \times I]/9.65 \times 10^5$$

where $G(-\text{ClO}^-)$ is the disappearance yield of ClO^- in molecule $(100 \text{ eV})^{-1}$, $\epsilon_{\text{ClO}^-}^\lambda$ is the mol extinction coefficient of ClO^- at wavelength λ and I is the absorbed dose in krad. $G(-\text{ClO}^-)$ was taken as 6.9 and 8.1 for N_2O and Ar saturated solutions respectively based on steady state radiolysis data to be presented later. The corrected spectra of the transient species are shown in fig. 1. For reasons to be discussed later this species is identified as ClO , produced by reaction (7).

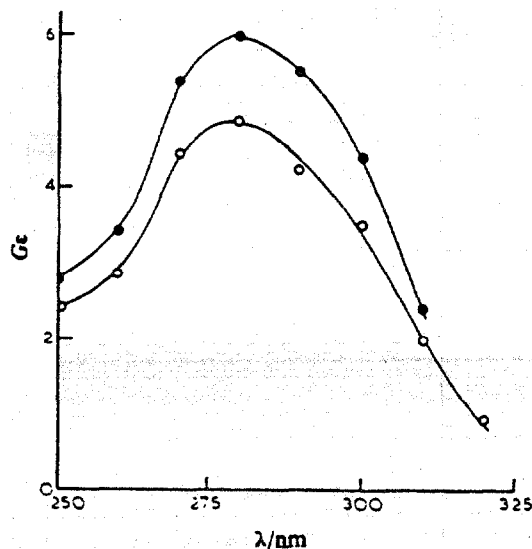
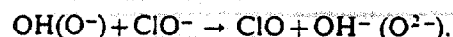


FIG. 1.—Absorption spectrum of ClO in aqueous solution at pH 11.4; (O) Ar saturated, (●) N_2O saturated. G = molecule $(100 \text{ eV})^{-1}$, ϵ = extinction coefficient in $\text{M}^{-1} \text{ cm}^{-1}$.

The values of $G(\text{ClO}) \epsilon_{\text{ClO}}^{280}$ are 4.8×10^3 and 6.0×10^3 for Ar and N_2O saturated solution respectively, and their relative magnitudes suggest that a product of reaction (8), which will occur in Ar saturated solution, is an oxidizing radical stoichiometrically equivalent to the hydroxyl radical.



KINETICS OF DECAY OF ClO

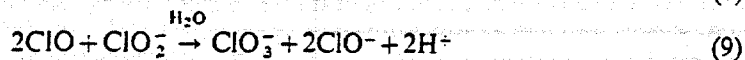
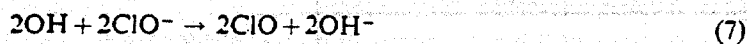
In N_2O saturated 10^{-3} M ClO^- solution at pH 11.4 the absorption due to ClO decayed and a permanent absorption remained. After correcting for the removal of ClO^- during the pulse a plot of $(D - D_\infty)^{-1}$ against time was linear (see fig. 2) where D and D_∞ are the optical densities due to ClO and the permanent product respectively. The first half-life of ClO was found to decrease with increasing dose per pulse, confirming the kinetics to be second order.

When $< 10^{-4} \text{ M}$ ClO_2^- was added to this system the rate of decay of ClO was

BEST AVAILABLE COPY

001627

enhanced but remained second order (see fig. 2). In this case D_{∞} was calculated from eqn (10) on the assumption that the following reactions occur



$$D_{\infty} = \Delta D_{\text{ClO}} - \Delta D_{\text{ClO}_2^-} \quad (10)$$

In eqn (10) $\Delta D_{\text{ClO}_2^-}$ is the change in optical density due to the removal of ClO_2^- after the pulse and is given by eqn (11) (cf. eqn (6))

$$\Delta D_{\text{ClO}_2^-} = [\frac{1}{2}G(-\text{ClO}^-)\epsilon_{\text{ClO}_2^-}^{\lambda} \times I]/9.65 \times 10^5 \quad (11)$$

The values of $2k/\epsilon$ obtained from the slopes of the plots exemplified in fig. 2 are given in table 2 and show that the dependence on $[\text{ClO}_2^-]$ is not simple.

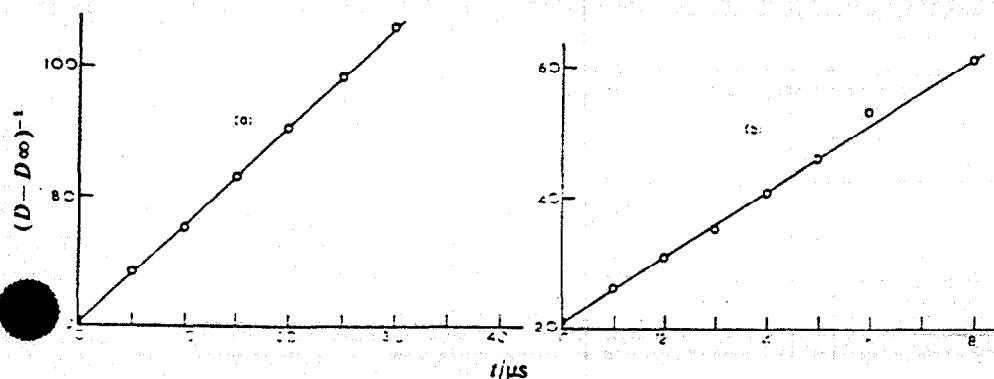


FIG. 2.—Decay of ClO at 280 nm, (a) in the absence of ClO_2^- , (b) in the presence of $5 \times 10^{-5} \text{ M ClO}_2^-$.

No chlorine dioxide was observed in these experiments, indicating that reaction (12) does not take place



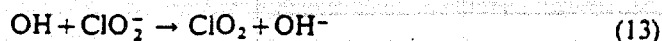
TABLE 2.—VALUES OF $2k/\epsilon$ FOR THE DECAY OF ClO IN THE ABSENCE AND PRESENCE OF ClO_2^- AT pH 11.4 AND 280 nm

$[\text{ClO}_2^-]/\text{M}$	$10^4 \times 2k/\epsilon/\text{cm s}^{-1}$ (a)	(b)
0	1.5 ± 0.1	1.6
2×10^{-5}	3.7 ± 0.2	3.7
5×10^{-5}	5.5 ± 0.4	5.9

(a) experimental value, (b) calculated value (see text).

ClO_2^- SOLUTIONS

On pulse radiolysis of N_2O saturated $10^{-3} \text{ M ClO}_2^-$ solution at natural pH, a permanent product was formed which was identified as ClO_2 by its absorption spectrum, and which must be produced by reaction (13).



Replacement of N_2O by Ar did not affect the yield of ClO_2 appreciably, showing that e_{aq}^- reacts with ClO_2^- to form a product which can oxidize ClO_2^- to ClO_2 .



001628

γ -RADIOLYSIS ClO^- SOLUTIONS

The yields of products of the γ -radiolysis of N_2O or Ar saturated or deaerated alkaline solutions of 10^{-3} M ClO^- are shown in table 3. All the measured yields were proportional to dose and their values are in excellent agreement with those obtained by Julien and Pucheault for neutral solution.⁷ No ClO_2^- was detected and $G(\text{Cl}^-)$ was calculated from the difference $G(-\text{ClO}^-) - G(\text{ClO}_3^-)$. In the absence of N_2O the material balance eqn for the quantities in table 3 in terms of oxygen content is (15).*

$$\frac{1}{2}G(\text{H}_2) + \frac{1}{2}G(-\text{ClO}^-) = \frac{3}{2}G(\text{ClO}_3^-) + G(\text{O}_2) \quad (15)$$

The data satisfy this eqn which demonstrates that no other oxygen containing product is formed.

TABLE 3.—PRODUCT YIELDS IN THE γ -RADIOLYSIS OF ALKALINE SOLUTIONS OF (a) 10^{-3} M ClO^- AND (b) 10^{-3} M $\text{ClO}^- + 10^{-4}$ M ClO_2^- $11.4 < \text{pH} < 12$

satürating gas	$G(-\text{ClO}^-)$	$G(-\text{ClO}_2^-)$	$G(\text{ClO}_3^-)$	$G(\text{H}_2)$	$G(\text{O}_2)$	$G(\text{Cl}^-)$
(a) { Ar or none	5.12 ± 0.05	0	1.03 ± 0.02	0.42 ± 0.02	1.20 ± 0.02	4.09
N_2O	3.30 ± 0.05	0	1.37 ± 0.05	—	—	1.93
(b) { Ar or none	3.62 ± 0.05	2.70 ± 0.05	2.63 ± 0.10	0.40 ± 0.01	0.70 ± 0.01	3.69
N_2O	1.70 ± 0.10	2.95 ± 0.05	2.87 ± 0.10	0.40 ± 0.01	0.69 ± 0.01	1.78

* $G(\text{Cl}^-)$ calculated from (a) $G(-\text{ClO}^-) - G(\text{ClO}_3^-)$, (b) $G(-\text{ClO}^-) + G(-\text{ClO}_2^-) - G(\text{ClO}_3^-)$.

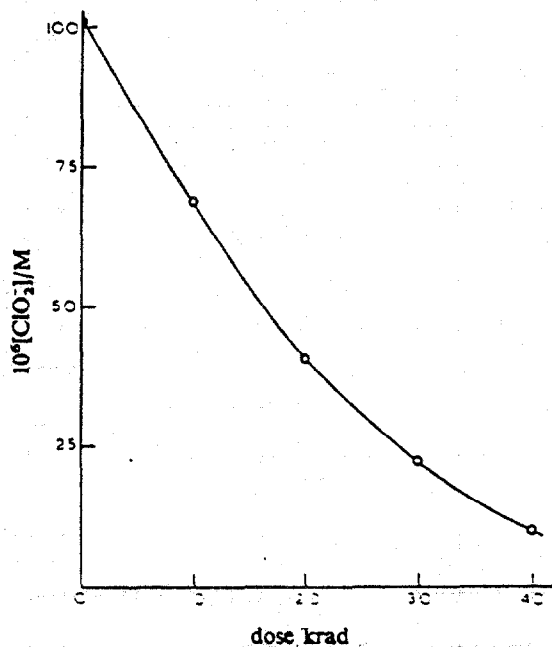


FIG. 3.—Variation of $[\text{ClO}_2^-]$ with dose in the γ -radiolysis of 10^{-3} M $\text{ClO}^- + 10^{-4}$ M ClO_2^- solution at pH 11.5.

BEST AVAILABLE COPY

001629

Also shown in table 3 are the yields when 10^{-4} M ClO_2^- was initially present in 10^{-3} M ClO^- solution. In this case the yields were proportional to dose for doses up to 20 krad. At larger doses $G(-\text{ClO}^-)$ and $G(\text{O}_2)$ increased while $G(-\text{ClO}_2^-)$ and $G(\text{ClO}_3^-)$ decreased. Evidently reactions which produce ClO_2^- must begin to occur when $[\text{ClO}_2^-]$ falls below 4×10^{-5} M (see fig. 3). Again the data for the Ar saturated and deaerated solutions are in accord with the material balance eqn for oxygen content (eqn (16)).*

$$\frac{1}{2}G(\text{H}_2) + \frac{1}{2}G(-\text{ClO}^-) + G(-\text{ClO}_2^-) = \frac{3}{2}G(\text{ClO}_3^-) + G(\text{O}_2) \quad (16)$$

ClO_2^- SOLUTIONS

Experiments were carried out to measure the yields of ClO_2 produced in the γ -radiolysis of ClO_2^- solutions at natural pH. The data are presented in fig. 4 and show that $G(\text{ClO}_2)$ decreases with increasing dose and decreasing $[\text{ClO}_2^-]$, the dose effect being more marked at the lower concentrations. ClO^- was also observed as a product but its yield was only measured quantitatively in Ar saturated 10^{-2} M ClO_2^- solution at pH 10 for a dose of 16 krad. Under these conditions $G(-\text{ClO}_2^-) = 7.8 \pm 0.1$, $G(\text{ClO}_2) = 5.4 \pm 0.1$ and $G(\text{ClO}^-) = 2.0 \pm 0.1$.

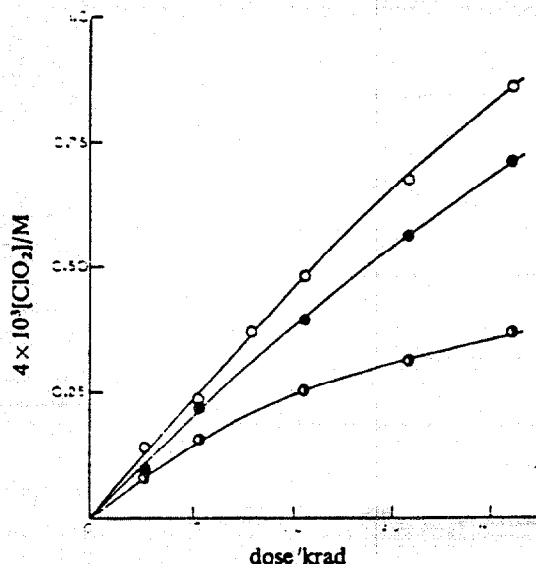
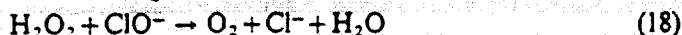


FIG. 4.—Dependence of ClO_2 yield on $[\text{ClO}_2^-]$ and dose: (○) 10^{-2} M, (●) 5×10^{-3} M, (○) 10^{-3} M ClO_2^- solution at natural pH saturated with N_2O .

REACTIVITY OF H_2O_2

Experiments were carried out to determine the relative reactivity of H_2O_2 with ClO^- and ClO_2^- . First 10^{-3} M ClO_2^- was added to 2×10^{-3} M H_2O_2 at pH 10 and the change in $[\text{ClO}_2^-]$ with time was measured. After 2 h less than 1 % of ClO_2^- had been destroyed. Next 10^{-4} M ClO^- was added to the $\text{ClO}_2^- + \text{H}_2\text{O}_2$ solution and was immediately destroyed. These observations, which are similar to those reported⁵ in the case of BrO^- and BrO_2^- , show that $k_{17} \ll k_{18}$.



* $\frac{1}{2}G(\text{H}_2)$ appears in eqn (15) and (16) because it is a measure of the amount of oxygen supplied by the solvent.

001630

DISCUSSION

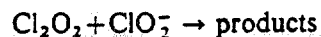
IDENTIFICATION OF ClO

The absorbing species produced in the pulse radiolysis of ClO^- solutions (fig. 1) is identified as ClO for the following reasons. First, it is produced by reaction of OH with ClO^- which is most likely to occur as reaction (7). Secondly, the absorption spectrum of ClO in the gas phase has maximum absorption at 290 nm. Thirdly, it has been pointed out by Amichai and Treinin¹⁷ that the transition energy of XO_n increase approximately linearly with the electronegativity of the halogen atom, which would place λ_{max} for ClO at about 280 nm since λ_{max} for BrO is 350 nm and for IO is 490 nm.¹⁷

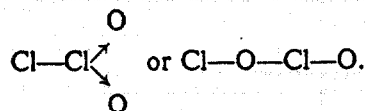
REACTIONS OF ClO AND Cl_2O_2

The enhancement of the rate of decay of ClO by ClO_2^- without change in kinetic order with respect to ClO or production of ClO_2 shows that reaction (12) does not take place. This is in contrast to the corresponding reaction in the bromine system which was found to be efficient.⁵ The electron affinities of ClO and ClO_2 are 2.89 and 3.14 eV respectively¹⁸ so that reaction (12) is unlikely on energetic grounds since changes in entropy and hydration energy are likely to be small.

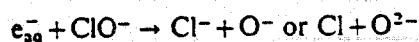
The observed decay kinetics of ClO are consistent with the occurrence of the following reactions



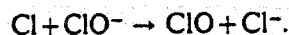
provided Cl_2O_2 does not absorb at 280 nm and equilibrium (19) is rapidly established. The dimer Cl_2O_2 has been suggested as an intermediate by Porter and Wright¹⁹ for the gas phase bimolecular decay of ClO , and by Taube and Dodgen²⁰ to account for the exchange of Cl between ClO^- and ClO_2^- in aqueous solution. Taube and Dodgen also proposed an asymmetrical structure for the dimer, viz.:



The data in fig. 1 indicate that reaction (8) occurs as



followed by (7) or (22)

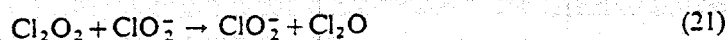
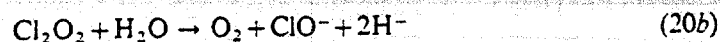
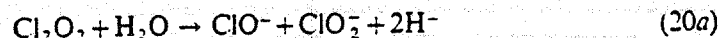


Because of the large electron affinity of Cl (3.8 eV) the first alternative seems the most likely. Hydrogen atoms are also likely to react rapidly with ClO^- , possibly according to reaction (23)



We conclude, therefore, that the oxygen containing products of the radiolysis of ClO^- solution, apart from the yield of oxygen arising from reaction (18), result from decomposition of Cl_2O_2 . The data in table 3 show these products are ClO_2^- and ClO_3^- and that added ClO_2^- increases the yield of the former and reduces the yield of the latter.

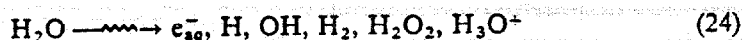
latter. These facts are consistent with reactions (20) and (21) taking place as follows



MECHANISM FOR THE RADIOLYSIS OF ClO^- SOLUTION

The complete mechanism for the radiolysis of ClO^- solution may now be written

as



followed by reactions (8), (23), (7), (19), (20a), (20b), (21) and (18). This mechanism predicts the following product yields in terms of the yields of the species formed in the radiolysis of water:

(a) In the absence of ClO_2^-

$$G(-\text{ClO}^-) = G(e_{aq}^-) + G(\text{H}) + G(\text{H}_2\text{O}_2) + G(\text{R}) \left(1 - \frac{3k_{20a} + k_{20b}}{4k_{20a} + 2k_{20b}} \right) \quad (25)$$

$$G(\text{ClO}_3^-) = G(\text{R}) / (4 + 2k_{20b}/k_{20a}) \quad (26)$$

$$G(\text{O}_2) = G(\text{H}_2\text{O}_2) + \frac{1}{2}G(\text{R}) / (1 + 2k_{20a}/k_{20b}) \quad (27)$$

where $G(\text{R}) = G(e_{aq}^-) + G(\text{H}) + G(\text{OH})$.

(b) In the presence of ClO_2^- , where reactions (20a) and (20b) are suppressed,

$$G(-\text{ClO}^-) = G(e_{aq}^-) + G(\text{H}) + G(\text{H}_2\text{O}_2) \quad (28)$$

$$G(\text{ClO}_3^-) = G(-\text{ClO}_2^-) = \frac{1}{2}G(\text{R}) \quad (29)$$

$$G(\text{O}_2) = G(\text{H}_2\text{O}_2). \quad (30)$$

Since $G(\text{O}_2) = 0.70 \pm 0.01$ for $5 \times 10^{-5} \text{ M} < [\text{ClO}_2^-] < 10^{-4}$ is equal to $G(\text{H}_2\text{O}_2)$ for dilute solutions²¹ we conclude that reaction (20b) is completely suppressed under these conditions. Similarly the constancy of $G(-\text{ClO}_2^-)$ over this concentration range (see fig. 3) is evidence of the suppression of reaction (20a). Substitution of the appropriate data in table 3 into eqn (28)-(30) gives $G(e_{aq}^-) + G(\text{H}) = 2.92 \pm 0.05$ and $G(\text{OH}) = 2.41 \pm 0.12$. These are in excellent agreement with the yields obtained from the hypobromite system²² and provide strong support for the proposed mechanism. On substituting these G values and the appropriate data in table 3 into eqn (26) and (27) we obtain $k_{20a}/k_{20b} = 1.69 \pm 0.20$ and 2.17 ± 0.11 respectively. The good agreement between these values provides further support for the mechanism. Taking $k_{20a}/k_{20b} = 1.93 \pm 0.24$ and the G values given above and substituting these in eqn (25) gives a calculated $G(-\text{ClO}^-) = 5.22 \pm 0.53$ which agrees well with the measured yield. On substituting for k_{20a}/k_{20b} and $G(\text{ClO}_3^-)$ for N_2O saturated solution (table 3) in eqn (26) we obtain $G(\text{R}) = 6.9 \pm 0.3$ in this case. This is the expected result since it is well established that under these conditions $G(e_{aq}^-) = G(\text{OH}) \sim 3.2$ and hence $G(\text{R}) \sim 7.0$.

001632

The decrease in $G(-\text{ClO}_2^-)$ when $[\text{ClO}_2^-]$ falls below $4 \times 10^{-5} \text{ M}$ indicates that reactions (20a) and (20b) begin to compete with (21) at this concentration. Applying the stationary state principle to $[\text{Cl}_2\text{O}_2]$ the proposed mechanism predicts that

$$\frac{-d[\text{ClO}_2^-]}{dt} = \frac{\frac{1}{2}G(R)I}{1 + \frac{k_{20b}}{k_{20a}} + \frac{k_{21}[\text{ClO}_2^-]}{k_{20a}}} \left(\frac{k_{21}[\text{ClO}_2^-]}{k_{20a}} - 1 \right) \quad (31)$$

where $G(R)I$ is expressed in M s^{-1} . Values of $-d[\text{ClO}_2^-]/dt$ at particular $[\text{ClO}_2^-]$ were obtained from the slope of the curve in fig. 3. Substitution of these together with the known values of $G(R)I$ and k_{20a}/k_{20b} in eqn (31) gives $k_{21}/k_{20a} = (1.3 \pm 0.6) \times 10^5 \text{ M}^{-1}$.

The predicted rate law for the decay of ClO is

$$-d[\text{ClO}]/dt = 2k_{19}[\text{ClO}]^2[1 - (1 + (k_{20a} + k_{20b} + k_{21}[\text{ClO}_2^-])/k_{-19})^{-1}]. \quad (32)$$

which, on writing k_{20a} and k_{21} in terms of k_{20b} , becomes

$$-d[\text{ClO}]/dt = 2k_{19}[\text{ClO}]^2[1 - (1 + (k_{20b}/k_{-19})(3.05 + 2.66 \times 10^5[\text{ClO}_2^-]))^{-1}]. \quad (33)$$

Thus the observed rate constant, $2k/\epsilon$ (see table 2) should be equal to

$$2k_{19}/\epsilon[1 - (1 + (k_{20b}/k_{-19})(3.05 + 2.66 \times 10^5[\text{ClO}_2^-]))^{-1}].$$

By a trial and error method good agreement was obtained between the observed and calculated rate constants with $2k_{19}/\epsilon = 1.65 \times 10^7 \text{ cm}^2 \text{ s}^{-1}$ and $k_{20b}/k_{-19} = 0.03$ (see columns 2 and 3 of table 2). Since $G(\text{ClO}) = G(R)$ we calculate $\epsilon_{\text{ClO}}^{280}$ to be $910 \text{ M}^{-1} \text{ cm}^{-1}$ and $875 \text{ M}^{-1} \text{ cm}^{-1}$ for Ar and N_2O saturated solutions respectively from the data in fig. 1 and the values of $G(R)$ given above. Using the mean value of ϵ we obtain $2k_{19} = 1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ which indicates that reaction (19) is close to the diffusion controlled limit.

The internal consistency of all the data discussed above is gratifying in view of the complexity of the reaction mechanism and is evidence of its validity.

MECHANISM FOR THE RADIOLYSIS OF ClO_2^- SOLUTION

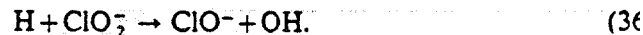
The dependence of $G(\text{ClO}_2)$ on dose and $[\text{ClO}_2^-]$ (see fig. 4) is consistent with reactions (34) and (35) taking place to an increasing extent as the ratio $[\text{ClO}_2]/[\text{ClO}_2^-]$ increases.



It is clear from the preceding discussion on the reactions of ClO that reaction (14) must produce O^-



to account for the yield of ClO_2 in Ar saturated solution. This mechanism would also explain the presence of ClO^- among the products, and is in contrast to the corresponding reaction in the bromine system where the products are BrO and O^{2-} . Hydrogen atoms are likely to react rapidly with ClO_2^- , possibly according to reaction (36).



Thus the mechanism for the radiolysis of ClO_2^- solutions may be written as reaction (24), (14), (36), (13), and (18), from which eqn (37)-(40) follow

BEST AVAILABLE COPY

001633

$$G(\text{ClO}_2) = G(\text{R}) \quad (37)$$

$$G(-\text{ClO}_2^-) = G(e_{aq}^-) + G(\text{H}) + G(\text{R}) \quad (38)$$

$$G(\text{ClO}^-) = G(e_{aq}^-) + G(\text{H}) - G(\text{H}_2\text{O}_2) \quad (39)$$

$$G(\text{O}_2) = G(\text{H}_2\text{O}_2). \quad (40)$$

The data in fig. 4 show that eqn (37) will be most nearly obeyed at high $[\text{ClO}_2^-]$ and low doses. From the initial slopes of yield-dose curves for 10^{-2} M ClO_2^- we obtain $G(\text{ClO}_2) = 5.5 \pm 0.05$ and 6.6 ± 0.05 in Ar and N_2O saturated solutions respectively. These are close to the values of $G(\text{R})$ derived from the corresponding ClO^- solutions and are in accord with the mechanism proposed above. Insufficient data have been obtained in this work to test eqn (38)-(40) because of the difficulty of measuring the initial values of $G(-\text{ClO}_2^-)$ and $G(\text{ClO}^-)$. However the yields observed at pH 10 for a dose of 16 krad are only slightly lower than those predicted by eqn (38) and (39).

M. S. S. thanks the Association of Commonwealth Universities for the award of a Scholarship.

¹ A. Treinin, *Israel J. Chem.*, 1970, 8, 103.

² M. Daniels, R. V. Meyers and E. V. Belardo, *J. Phys. Chem.*, 1968, 72, 389.

³ G. Zimmerman, *J. Chem. Phys.*, 1955, 23, 825.

⁴ J. Barrett, M. F. Fox and A. L. Mansell, *J. Phys. Chem.*, 1965, 69, 2996.

⁵ G. V. Buxton and F. S. Dainton, *Proc. Roy. Soc. A*, 1968, 304, 427.

⁶ O. Amichai, G. Czapski and A. Treinin, *Israel J. Chem.*, 1969, 7, 351.

⁷ L. Julien and J. Pucheault, *J. Chim. Phys.*, 1967, 64, 725.

⁸ L. T. Bugaenko, E. P. Kalyazin and N. K. Bakh, *Russ. J. Phys. Chem.*, 1960, 34, 594.

⁹ R. L. Taylor and C. Bostock, *J. Chem. Soc.*, 1912, 444.

¹⁰ K. W. Chambers, E. Collinson, F. S. Dainton, W. A. Seddon and F. Wilkinson, *Trans. Faraday Soc.*, 1967, 63, 1699.

¹¹ G. V. Buxton, F. S. Dainton and J. Kalcinski, *Int. J. Radiat. Phys. Chem.*, 1969, 1, 87.

¹² I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis* (MacMillan, London, 1950), p. 627.

¹³ A. O. Allen, C. J. Hochanadel, J. A. Glormley and T. W. Davis, *J. Phys. Chem.*, 1952, 56, 575.

¹⁴ L. J. Csanyi and M. Szabo, *Talanta*, 1958, 1, 359.

¹⁵ G. V. Buxton, *Trans. Faraday Soc.*, 1969, 65, 2150.

¹⁶ R. A. Durie and D. A. Ramsay, *Canad. J. Phys.*, 1958, 36, 35.

¹⁷ O. Amichai and A. Treinin, *J. Phys. Chem.*, 1970, 74, 830.

¹⁸ V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, *Bond Energies, Ionisation Potentials and Electron Affinities* (Arnold, London, 1966).

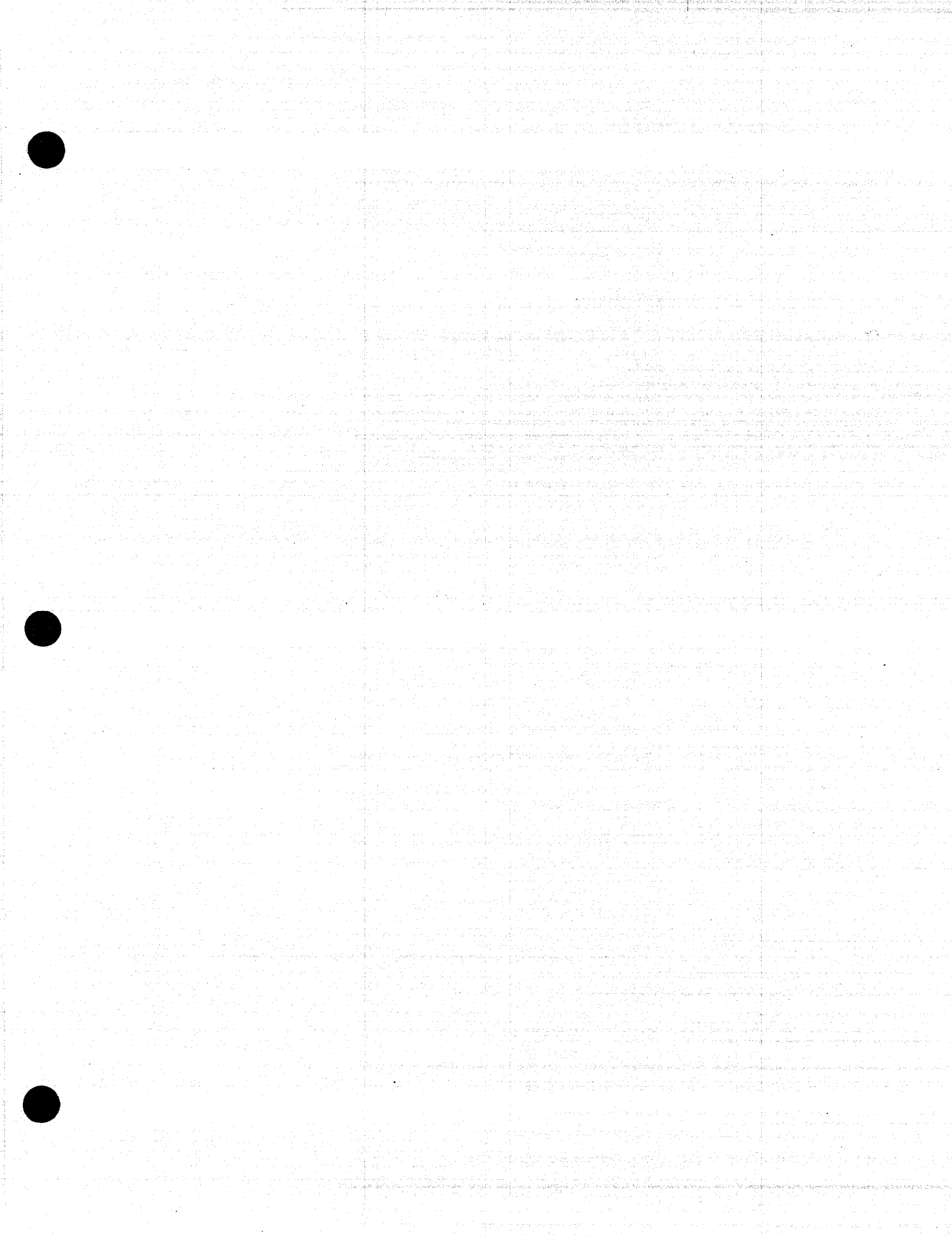
¹⁹ G. Porter and F. J. Wright, *Disc. Faraday Soc.*, 1953, 14, 23.

²⁰ H. Taube and H. Dodgen, *J. Amer. Chem. Soc.*, 1949, 71, 3330.

²¹ A. O. Allen, *The Radiation Chemistry of Water and Aqueous Solutions* (Van Nostrand, New York, 1961).

²² G. V. Buxton and F. S. Dainton, *Proc. Roy. Soc. A*, 1968, 304, 441.

001634





Photodecomposition of Chlorine Dioxide and Sodium Chlorite in Aqueous Solution by Irradiation with Ultraviolet Light

MATERIALS MAY BE
PROTECTED BY
(TITLE 17, U.S. CODE)

Hervé Cosson and William R. Ernst*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Rates of reaction and product formation were measured in photodecomposition experiments of aqueous sodium chlorite at 253.7 nm in a reactor that was continuously sparged with nitrogen to remove chlorine dioxide. Rapidly removing chlorine dioxide greatly reduced the formation of chlorate. The results of this work suggest that chlorate is not formed by direct decomposition of chlorite, but rather by decomposition of chlorine dioxide. The results are consistent with the stoichiometry, $3\text{ClO}_2^- + \text{H}_2\text{O} (+h\nu) \rightarrow \text{Cl}^- + 2\text{ClO}_2 + 2\text{OH}^- + 0.5\text{O}_2$. The rate of photodecomposition of sodium chlorite was studied over a pH range of 4–10 and at unbuffered conditions. Distribution of major products was not affected by pH; rates of reaction and chlorine dioxide formation were maximum at pH 6. Results of this work provide indirect evidence of the validity of certain elementary steps in mechanisms that have been proposed by previous workers. Quantum yields were measured for both photodecomposition of chlorine dioxide and sodium chlorite. For the former reaction, the values were 0.44 at 253.7 nm and 1.4 at 300 nm. For the latter reaction, the values at 253.7 nm ranged from 0.72 to 1.53, depending upon pH. Corresponding quantum yields for formation of chlorine dioxide ranged from 0.43 to 0.94, depending upon pH.

Introduction

Chlorine dioxide is primarily used as an oxidizing agent in the treatment and bleaching of wood pulp, in water treatment, in textiles and wool treatment (bleaching), and in the treatment of flour and of food products. Chlorine dioxide can be produced by several methods. It can be prepared either by reduction of chlorates or by oxidation of chlorites.

In large-scale commercial pulp bleaching operations, chlorine dioxide is produced by reducing chlorate in strong acid solution (Rapson, 1956, 1958; Rapson and Wayman, 1949, 1954; Holst, 1945; Persson, 1945; Day and Fenn, 1949; Rosen, 1976; Engström and Norell, 1992; Engström and Falgén, 1992). Variations of this process depend upon the type of acid (hydrochloric or sulfuric acid), operating acidity, and choice of reducing agent (methanol, sulfur dioxide, sodium chloride, hydrogen peroxide). All of these variables affect the chemistry of the process. Both final product and byproducts vary significantly depending on the set of operating conditions and choice of reducing agent.

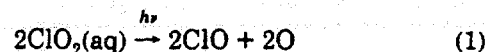
In water treatment, chlorine dioxide is produced by oxidation of chlorite. This operation is carried out on a much smaller scale and does not require equipment as extensive as that required for a chlorate reduction process. Usually a solution of sodium chlorite is mixed with a strong solution of chlorine in water yielding chlorine dioxide and chloride. Oxidizing agents such as ozone or persulfates can also be used instead of chlorine.

Recently, several workers have studied an alternative way of producing chlorine dioxide. This process involves irradiation of an aqueous solution of sodium chlorite with ultraviolet light. The process is simple in terms of procedures and apparatus. The chlorine dioxide that is formed can be recovered in either gaseous or liquid phase, depending upon the purpose of the operation. This process requires only a single reactant, sodium chlorite, and the reaction can be terminated at any time by extinguishing the UV source.

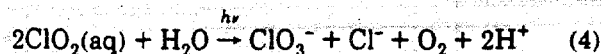
Several patents have been filed concerning methods of generating chlorine dioxide (Fisher, 1983, 1984; Callera, 1989; Sekisui Plastics Co. Ltd., 1991) by photodecomposition of sodium chlorite with ultraviolet light. One of the potential drawbacks of this process is that chlorine dioxide decomposes when irradiated. Therefore chlorine dioxide must be recovered continuously from the reactor solution. Chlorine dioxide is produced in the aqueous phase, but can be gasified by sparging nitrogen or air through the solution.

Variations of reactors have been studied. Ultraviolet emitting lamps can be placed inside (Callera, 1989) or outside (Fisher, 1983, 1984) the reactor. In the latter case, the reactor is constructed of quartz, Suprasil, or Vycor in order not to absorb ultraviolet light.

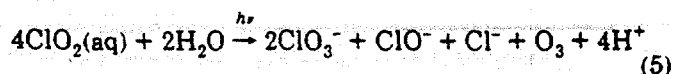
Photodecomposition of Chlorine Dioxide. Little work has been published on the continuous photolysis of chlorine dioxide in aqueous solution. The following mechanism has been proposed for wavelengths between 300 and 436 nm (Bowen and Cheung, 1932):



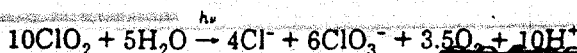
and the overall reaction is



Zika *et al.* (1984) proposed a different mechanism initiated by the same primary photoreaction, but leading to a different overall reaction and product distribution:



Recently Karpel Vel Leitner *et al.* (1992a) proposed an overall reaction for the decomposition of chlorine dioxide in water at 253.7 nm.



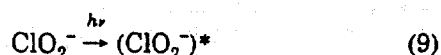
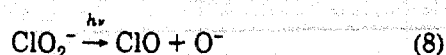
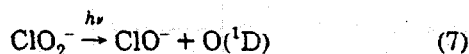
* Author to whom correspondence should be addressed.

This global reaction is the result of a series of complex intermediate reactions initiated by ultraviolet radiation.

The quantum yield of chlorine dioxide photodecomposition in water has been briefly investigated (Bowen and Cheung, 1932; Zika *et al.*, 1984; Karpel Vel Leitner *et al.*, 1992b). The first two of these research groups showed that the value of the quantum yield increases with decreasing wavelength. Recently, Zika *et al.* (1984) obtained a value of 1.4 at 300 nm and pH 7, while previous workers (Bowen and Cheung, 1932) reported a value of 1. These quantum yields are reported for the overall decomposition of chlorine dioxide, and it must be pointed out that primary quantum yield of decomposition is still unknown. No information on the quantum yield of chlorine dioxide decomposition at 253.7 nm was reported by any of these authors.

Photodecomposition of Sodium Chlorite. Buxton and Subhani (1972a,b) have studied the photochemistry of oxychlorine ions. In particular, they focused their attention on the photodecomposition of aqueous solutions of chlorite ions (1972b). The products they observed in steady state photolysis experiments at pH 10 were ClO^- , ClO_2 , Cl^- , O_2 , and little ClO_3^- . In their experimental procedure, chlorine dioxide was removed from the reactor solution at frequent intervals.

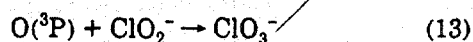
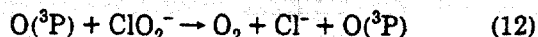
They proposed the following primary photodecomposition reactions at 254 nm:



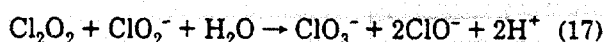
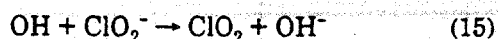
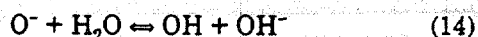
Reaction 7 leads to the following secondary reactions:



At 365 nm, some oxygen may also be formed in the (^3P) state. This will lead to the following reactions:



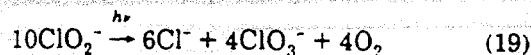
Reaction 8 leads to the following secondary reactions:



In reaction 9, $(\text{ClO}_2^-)^*$ is a long-lived triplet state of chlorite ion. It reacts with another chlorite ion.



Karpel Vel Leitner *et al.* (1992a,b) studied the photodecomposition of sodium chlorite in solution at 253.7 nm. They showed that chloride and chlorate were the major products of the decomposition. They proposed the following overall reaction:



In their study, chlorine dioxide is considered as an intermediate product and is left in the reactor solution where it undergoes decomposition. In the second part of the study (1992b), they determined a value of 1 for the quantum yield of decomposition of sodium chlorite at natural pH.

The quantum yield for the disappearance of ClO_2^- at 253.7 nm was found experimentally (Buxton and Subhani, 1972b) to be 0.50 at pH 10 and 0.79 at natural pH. The quantum yield for the production of chlorine dioxide was respectively 0.24 and 0.41 at these pH values.

The present study was designed to achieve a better understanding of the production of chlorine dioxide by irradiation of sodium chlorite with ultraviolet light, especially in terms of stoichiometry, final stable products, and relative rates of production of products and byproducts. This understanding would enable us to determine the maximum yield of chlorine dioxide that can be achieved. We propose a mechanism which explains our experimental results and is consistent with previous work. Our experimental approach involved generating chlorine dioxide while simultaneously removing it from the reaction solution. This approach was aimed at minimizing further reaction of chlorine dioxide and thereby maximizing the ratio of chlorine dioxide to reacted chlorite.

Experimental Section

001636

Photodecomposition of Chlorine Dioxide in Solution. A. Photochemical Chamber Reactor. For this study we used a photochemical chamber reactor equipped with a maximum of 12 low-pressure mercury lamps. This homemade reactor is similar to a Rayonet Chamber Reactor RPR 100 (The Southern New England Ultraviolet Co., Branford, CT). The reactor was previously constructed and loaned to us by Dr. L. Tolbert of the Georgia Institute of Technology School of Chemistry.

The reactor body is a cylindrical chamber 25.4 cm in diameter and 30 cm deep with 12 lamps aligned vertically at the wall. The chamber is cooled by a fan at the bottom, which allows for normal operating temperature between 25 and 30 °C. An external power supply contains the starters and a switch. The reactor can be operated with fewer lamps by removing some of them from their plugs. When fewer than 12 lamps were used, the remaining lamps were arranged symmetrically so as to ensure a uniform and symmetric exposure to the ultraviolet radiation. The walls are made of polished aluminum, which provides good reflection. When 12 lamps are used, the total power consumption (including the fan) approximately 240 W.

We used germicidal low-pressure mercury lamps of type G8T5 (G.E. and Westinghouse), which provide an intense source of ultraviolet light. The mercury line radiates at 253.7 nm and accounts for approximately 90% of the energy radiated in the 250–600-nm region. We also used phosphor-coated low-pressure mercury lamps emitting at 300 nm, purchased from The Southern New England Ultraviolet Co.

B. Reaction Vessel. The reaction vessel (shown in Figure 1, within the photochemical reaction chamber) is a 38-cm-long and 3.8-cm-diameter cylindrical vessel, designed specifically for this study. The vessel is made of quartz with a thickness of 1 mm. This thickness ensures approximately 90% transmission down to a wavelength of 200 nm (Calvert, 1967; Koller, 1952). The vessel was suspended in the center of the photochemical chamber by a clamp.

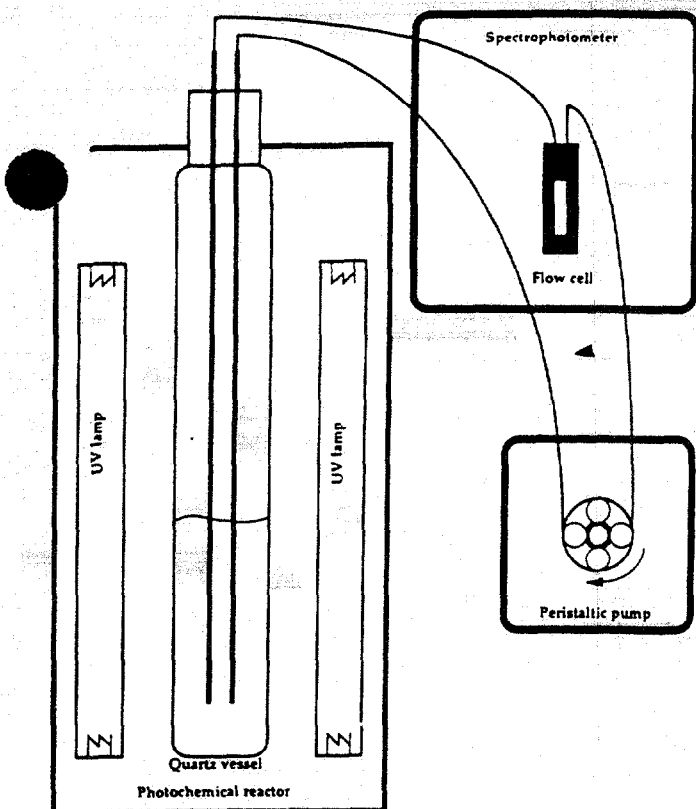
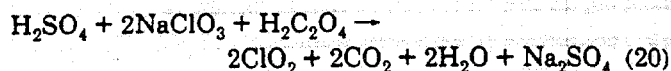


Figure 1. Experimental apparatus for the study of chlorine dioxide photodecomposition.

C. Chlorine Dioxide Solution. Aqueous solutions of chlorine dioxide were prepared by us using a simple procedure based on the reaction of sodium chlorate with sulfuric acid in the presence of sulfuric acid (Masschelein, 1979). This reaction is reported to produce pure chlorine dioxide with no contamination by chlorine. The preparation is based on the following stoichiometry:



The experimental apparatus consists of a 200-mL volumetric flask and three absorbers connected in series. The reactants were fed into the flask, and the mixture was stirred at ambient temperature. The gaseous products exited the reactor and traveled through the first absorber where chlorine was trapped in dibasic sodium phosphate and then through the second absorber where most of the chlorine dioxide was collected in distilled water at near freezing temperature. The third absorber contained distilled water and trapped chlorine dioxide which escaped the previous absorber.

This setup allowed us to prepare a stock solution of 0.1 M chlorine dioxide (7 g/L). Stored in a brown bottle in a refrigerator, the chlorine dioxide solution is stable and can be used for up to 1 week without detectable decomposition products.

D. Irradiation Procedure. In the study of chlorine dioxide decomposition we irradiated a chlorine dioxide solution while continuously monitoring the absorbance and thus the concentration in chlorine dioxide (Figure 1). In a typical experiment, the reaction vessel was filled with 100 mL of chlorine dioxide solution; the solution was irradiated and pumped continuously through a 1-mm path length flow cell in a Milton Roy Spectronic 1201 spectrophotometer while the absorbance was monitored at 370 nm. The solution exiting the cell returned to the reactor. The movement of the solution also ensured its mixing. At 370 nm the extinction coefficient of chlorine dioxide in

solution is $104 \text{ M}^{-1} \text{ mm}^{-1}$. The volume of solution circulating in the tubes at any given time was approximately 30 mL, and the pumping rate was 2 mL/s. All experiments were run between 23 and 25 °C.

We used two wavelengths for irradiation, 300 and 253.7 nm. At 253.7 nm we examined the decomposition of chlorine dioxide as a function of the ultraviolet intensity by varying the number of lamps in the chamber. We used configurations with 12, 8, 6, 4, 2, and 0 lamps. With 0 lamps, the solution was exposed to ambient light only. Several experiments were run for each configuration. To improve accuracy, we used relatively high initial chlorine dioxide concentration (0.020–0.024 M), which ensured that the solution would capture a large fraction of the incident UV light.

Photodecomposition of Sodium Chlorite in Solution at 253.7 nm. A. Choice of Ultraviolet Wavelength. Because UV light decomposes both chlorite and chlorine dioxide, an early task was to find a wavelength at which the coefficient of molecular extinction is minimum for chlorine dioxide (low absorption and therefore little tendency to react) and maximum for sodium chlorite (high absorption and therefore high tendency to react).

Absorption spectra of aqueous solutions of chlorine dioxide and sodium chlorite were determined for the wavelength range of 230–370 nm using a Milton Roy Spectronic 1201 spectrophotometer. The sodium chlorite spectrum was obtained from very stable absorbance of 0.0101 M NaClO_2 at pH 11 and 25 °C. The chlorine dioxide spectrum was obtained from 0.0017 M ClO_2 at 25 °C. The extinction coefficient for chlorine dioxide shows a minimum at about 270 nm and that for chlorite a maximum at about 270 nm. Therefore 270 nm would be the optimal wavelength for these experiments.

We chose to use low-pressure mercury lamps emitting at 253.7 nm since they are readily available. This wavelength is sufficiently near the optimal value of 270, and has been used in various patents and other references (Fisher, 1983, 1984; Callerame, 1989; Buxton and Subhani, 1972b) claiming methods for generating chlorine dioxide by irradiation of sodium chlorite.

B. Sodium Chlorite Solution. Sodium chlorite was prepared from Aldrich technical grade sodium chlorite (80%) following the procedure described by Peintler and Nagypal (1990). The carbonate content was precipitated with BaCl_2 solution. The excess Ba^{2+} ions were eliminated by adding a calculated amount of Na_2SO_4 solution. The resulting NaClO_2 was recrystallized twice from an 80% ethanol–water mixture at low temperature. This procedure yielded NaClO_2 with a chloride concentration of less than 0.7%. Sodium chlorite stock solution was prepared by diluting sodium chlorite crystals with distilled water, and was kept at room temperature in the dark to avoid any decomposition due to the ambient light.

C. Experimental Apparatus and Procedure. The experimental apparatus consists of a quartz reaction vessel within a photochemical reaction chamber equipped with low-pressure mercury lamps emitting at 253.7 nm, and an absorption vessel. The quartz vessel and photochemical reaction chamber are those shown in Figure 1; however, the liquid recirculation tubing, pump and spectrophotometer were replaced by a gas absorption system. It consists of gas inlet and outlet tubing that extends through the top of the quartz vessel. Outside the vessel, the inlet tube connects to a nitrogen cylinder; inside it extends below the liquid surface where it connects to a glass frit near the bottom of the vessel. The outlet tube extends from the gas space in the quartz vessel through the top and connects to a gas bubbler containing an absorbing liquid.

The quartz vessel was filled with 70 mL of 0.1 M sodium chlorite solution and irradiated. Chlorine dioxide was sparged continuously from the reactor by a stream of nitrogen (UHP grade, Holox Ltd.) which then passed either directly to the vent or through the absorber which was filled with a 10% potassium iodide solution buffered at pH 9 with sodium phosphate. Chlorine dioxide reacted with iodide to give iodine, and nitrogen was vented to the hood.

The procedure involved making several runs with different irradiation times, titrating for the various chemicals in the reactor solution, and determining chlorine dioxide and chlorine production by titrating the absorber solution.

The reactor solution was analyzed for hydroxide by titration with standard acid solution (Rand *et al.*, 1975), for chloride by acidifying and titrating with standard silver nitrate solution (Rand *et al.*, 1975), and for chlorate, chlorite, and hypochlorite by the titration procedure of Aieta *et al.* (1984). In this latter method, sodium thiosulfate is used to titrate iodine that is formed when potassium iodide is added to a sample that contains the chlorine-containing species. Sample pretreatments and pH adjustments are used to differentiate among the various chlorine-containing species. This method also detects chlorine dioxide; however, there was no chlorine dioxide left in the vessel because it was removed by the continuous, high nitrogen flow ($4000 \text{ cm}^3/\text{min}$). To further confirm there was no residual chlorine dioxide, we checked the final absorbance of the reactor solution at 370 nm and found it to be negligible. Iodine formed in the absorber was titrated with thiosulfate at pH 7 and pH 2, using the method of Aieta *et al.* (1984). The mols of chlorine dioxide and chlorine were then divided by the reactor solution volume in order to express their concentrations in terms of reactor volume.

We examined the influence of several variables on the rate of production and on the stoichiometry of the reaction. These variables were nitrogen sparging flow rate, pH of the chlorite solution, and initial chlorite concentration in the reactor solution.

Quantum Yield of Photodecomposition. In this study the quantum yield of photodecomposition is defined as the number of molecules decomposed (chlorine dioxide or sodium chlorite) divided by the number of photons absorbed by the solution. Therefore two separate measurements were required to calculate each quantum yield. The rate of photodecomposition of chlorine dioxide or sodium chlorite was obtained from our experiments. To determine the number of photons absorbed by the solution, we used chemical actinometry with potassium ferrioxalate. We followed the technique described by Hatchard and Parker (1956).

Results and Discussion

Photodecomposition of Chlorine Dioxide in Aqueous Solution. Figure 2 shows the results of the irradiation of chlorine dioxide at 253.7 and 300 nm. The absorbance of the reactor solution measured at 370 nm is recorded versus time of irradiation. In the experiment run without lamps the chlorine dioxide solution was exposed to ambient light. For safety reasons, the vessel was not sealed; therefore, a portion of the chlorine dioxide disappearance can be attributed to evaporation.

This graph shows that ultraviolet radiation has a strong effect on the stability of chlorine dioxide. Irradiation causes a fast decomposition at a rate varying with the number of lamps used, and therefore with the flux of ultraviolet light absorbed by the solution.

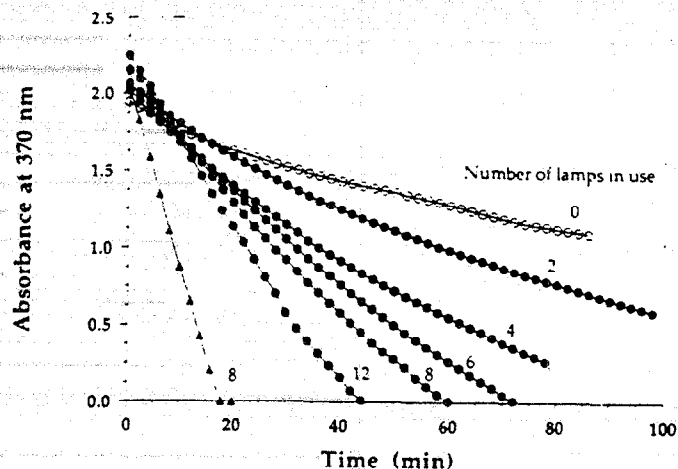


Figure 2. Photodecomposition of chlorine dioxide. Absorbance at 370 nm versus time. Irradiation at 253.7 nm (●), 300 nm (▲), and ambient light (○). Flow cell with 1 mm path length.

Figure 2 shows that during about the first 10 min of each experiment the rate of decomposition was constant. We determined the rates based on the first 10 min of each experiment by fitting these data with straight lines. The slope of each line is the rate of decomposition in absorbance units per minute which we transformed to a rate in molar per minute using the extinction coefficient of chlorine dioxide at 370 nm ($104 \text{ M}^{-1} \text{ mm}^{-1}$). Table 1 summarizes the rate of decomposition corresponding to each configuration and each wavelength.

Quantum Yield of Chlorine Dioxide Decomposition. Using rates of decomposition and ultraviolet flux determined by chemical actinometry, we calculated the quantum yield of chlorine dioxide decomposition. Rates of decomposition were corrected by subtracting the contribution due to the ambient light. The incident photon flux due to the ambient light was very small compared to the flux emitted by the lamps, and no correction was necessary.

Table 2 shows that at 253.7 nm we found an average quantum yield of 0.42. At 300 nm we found a quantum yield of 1.38. This value is in very good agreement with the value of 1.40 given by Zika *et al.* (1984), and higher than the value of 1 given by Bowen and Cheung (1932). As stressed by Zika *et al.* (1984), this latter value may be underestimated due to the broad spectral region (316–270 nm) used.

Photodecomposition of Sodium Chlorite in Aqueous Solution. A. Unbuffered Chlorite Solutions. A first set of experiments was conducted with unbuffered solutions of sodium chlorite. The initial chlorite concentration was between 0.09 and 0.1 M, with a chloride concentration below 0.001 M and a chlorate concentration below 0.001 M. After 60 min of irradiation the final pH was about 12.6, indicating the formation of OH^- . The reactor solution was continuously sparged with nitrogen at $4000 \text{ cm}^3/\text{min}$ to remove chlorine dioxide.

We titrated the reactor solution for Cl^- , ClO_2^- , OH^- , ClO_3^- , and ClO^- and titrated the absorber solution for ClO_2 and Cl_2 . Typical evolution of reactor species concentration is shown in Figure 3. Chlorite concentration is shown as moles of chlorite reacted per liter. Chlorate and hypochlorite are not shown but were titrated at the end of each run. No perchlorate was found in the reactor solution.

Hydroxide was titrated and the pH of the reactor solution was calculated. Product concentrations (and consumed chlorite) are shown in Figure 4 as a function of the irradiation time. After several runs we were able to determine an average rate of production for each product.

Table 1. Rate of Decomposition of Chlorine Dioxide for Various Lamp Configurations

wavelength (nm)	ambient	253.7	253.7	253.7	253.7	253.7	300
no. of lamps	0	2	4	6	8	12	8
rate of decompn (M/min) $\times 10^3$	0.169	0.240	0.315	0.335	0.427	0.551	1.009

Table 2. Quantum Yield of Chlorine Dioxide Decomposition at 253.7 and 300 nm

wavelength (nm)	ambient	253.7	253.7	253.7	253.7	253.7	300
no. of lamps	0	2	4	6	8	12	8
rate of photon abs (M/min) $\times 10^3$	0	0.182	0.354	0.394	0.583	0.876	0.674
rate of ClO ₂ decompn (M/min) $\times 10^3$	0.169	0.240	0.315	0.335	0.427	0.551	1.009
quantum yield of decompn		0.39	0.41	0.42	0.44	0.44	1.38

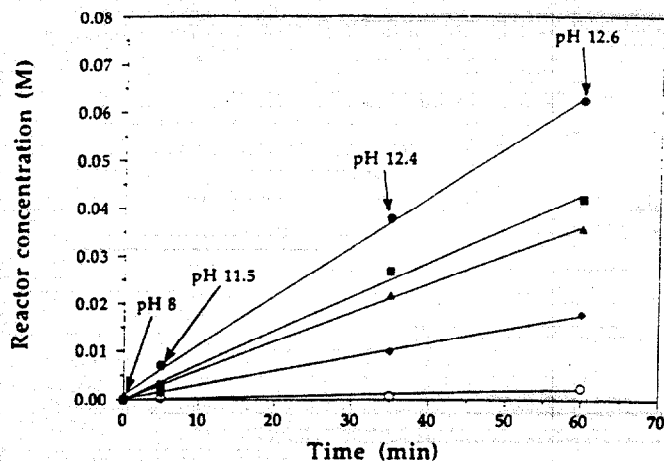


Figure 3. Photodecomposition of sodium chlorite in solution. Evolution of reactor species and absorber species concentrations for unbuffered solutions. ClO₂-reacted (●), ClO₂ (▲), Cl⁻ (◆), OH⁻ (■), Cl₂ (○). Twelve lamps in use.

Table 3. Irradiation of Sodium Chlorite. Average (Based on Three Runs) Rate of Production in the Case of Unbuffered Experiments. Twelve Lamps in Use

product	rate of production (M/min) $\times 10^3$	product yield (M/M of chlorite reacted)
ClO ₂ -reacted	0.97 \pm 0.048	100
ClO ₂	0.58 \pm 0.030	60 \pm 3
Cl ⁻	0.29 \pm 0.040	30 \pm 4
OH ⁻	0.69 \pm 0.048	71 \pm 5
Cl ₂	0.02 \pm 0.015	2 \pm 2
ClO ⁻	0.05 \pm 0.005	5 \pm 0.5
ClO ₃ ⁻	0.04 \pm 0.005	4 \pm 0.5

and average proportion of each product compared to the amount of chlorite reacted. We calculated these proportions by forming the ratio of the product rate to the chlorite rate of dissociation. Data are summarized in Table 3.

Hydroxide, chlorine dioxide, and chloride appear to be the major products of the decomposition of sodium chlorite. Chlorate and hypochlorite appear in lesser amounts. Chlorine appears in minor quantity, and the rate of production seems to fluctuate with time.

B. Effect of pH on the Photodecomposition of Sodium Chlorite. We studied the photodecomposition of sodium chlorite solution buffered at various pH values. The solutions were prepared by first dissolving sodium chlorite in 0.2 M sodium phosphate solution yielding a solution with pH slightly above 9. Then we adjusted the pH to the desired value by slowly adding 1 M sulfuric acid. We studied solutions with pH ranging from 4 to 10. Below pH 4, sodium chlorite solutions tend to decompose rapidly even in the absence of light, by disproportionation. The pH value of 10 was achieved by buffering with 0.1 M sodium carbonate and adjusting the pH with sodium bicarbonate.

In this set of experiments, the nitrogen flow rate was set at 4000 cm³/min and 12 lamps were operated. The initial chlorite concentration was between 0.09 and 0.1 M.

After irradiation, we titrated for reactor species as before. The sum of chlorate and hypochlorite rates was determined

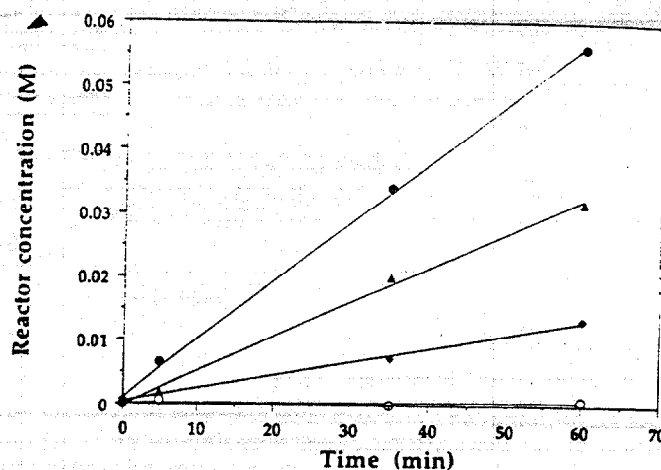


Figure 4. Photodecomposition of sodium chlorite in solution. Evolution of reactor species and absorber species concentrations at pH 10. ClO₂-reacted (●), ClO₂ (▲), Cl⁻ (◆), Cl₂ (○). Twelve lamps in use.

Table 4. Irradiation of Sodium Chlorite. Average (Based on Three runs) Rate of Production and Product Yields in the Case of Buffered Experiments. Twelve Lamps in Use

species	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	average
Rate of Production (M/min) $\times 10^3$								
ClO ₂ -reacted	1.56	1.79	1.92	1.48	1.15	0.95	0.90	
ClO ₂	1.00	1.15	1.18	0.84	0.67	0.59	0.54	
Cl ⁻	0.42	0.47	0.53	0.47	0.38	0.24	0.21	
Cl ₂	0.05	0.07	0.02	0.03	0.02	0.00	0.01	
ClO ₃ ⁻ and ClO ⁻	0.05	0.04	0.19	0.10	0.046	0.11	0.14	
Product Yield (M/M of Chlorite Reacted)								
ClO ₂ -reacted	100	100	100	100	100	100	100	100
ClO ₂	64	64	61	57	59	62	60	61
Cl ⁻	27	26	27	32	33	26	23	28
Cl ₂	3	4	1	2	2	0	1	2
ClO ₃ ⁻ and ClO ⁻	3	2	10	7	4	12	15	8

by difference to achieve a chlorine balance. The reactor solution showed a very slight change in pH. Figure 4 shows the evolution of reactor products during a run at pH 10.

Table 4 shows average rates of production and product yields at various pH conditions. Chlorine dioxide and chloride yields are reasonably constant, and pH does not seem to have a significant effect on them. However the rate at which sodium chlorite reacts is affected by the pH of the reactor solution. A maximum rate appears at a pH value of 6. Figure 5 shows the rate of formation of chlorine dioxide versus pH of the chlorite solution. Compared to this curve, the rate of formation in the case of unbuffered chlorite solutions seems to be consistent, as the pH was above 12 throughout most of the unbuffered experiments.

C. Stoichiometry and Mechanism of the Photodecomposition of Sodium Chlorite. Our results show that when we varied pH, the product distribution, hence the stoichiometry of the overall reaction to the major products, Cl⁻, ClO₂, and OH⁻, remained reasonably constant even though the overall reaction rate varied significantly. This result provides indirect evidence about the mechanistic steps of the process: that the stoichiometry of the overall reaction is fixed by the elementary steps of the mechanism.

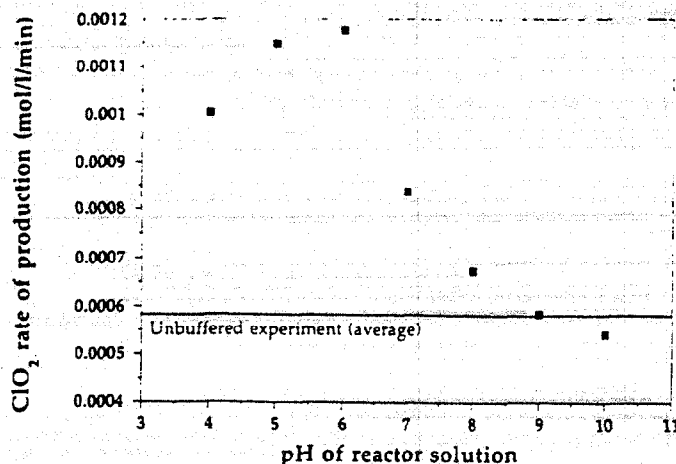


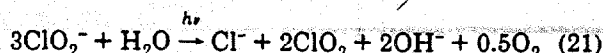
Figure 5. Rate of formation of chlorine dioxide at various pH values and in the case of unbuffered solutions.

and that the steps are interdependent in such a way that they do not allow for independent production of the products, Cl^- , ClO_2 , and OH^- .

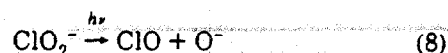
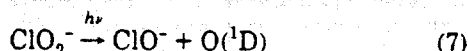
Karpel Vel Leitner *et al.* (1992a,b) studied the photodecomposition of chlorine dioxide and sodium chlorite in aqueous solution by irradiation at 253.7 nm. They used a similar reactor and low-pressure mercury lamps; however in their work chlorine dioxide was not sparged from the reactor, but was subject to decomposition. In a first set of experiments, they studied the decomposition of chlorine dioxide and determined that chloride and chlorate were the major decomposition products. They reported yields of 0.4 mol of chloride and 0.6 mol of chlorate per mole of reacted chlorine dioxide. In a second set of experiments they studied the decomposition of sodium chlorite. Chloride and chlorate were also the major decomposition products, reported at yields of 0.6 mol of chloride and 0.4 mol of chlorate per mole of reacted chlorite.

We will use our results and the results of others in proposing a stoichiometry and a mechanism for the photodecomposition of chlorite. We will show that our results are consistent with those of Karpel Vel Leitner *et al.* (1992a) if we assume that chlorate forms only from chlorine dioxide. We will refer to other studies (Karpel Vel Leitner *et al.*, 1991, 1992a,b; Buxton and Subhani, 1972a,b) to explain the presence of hypochlorite.

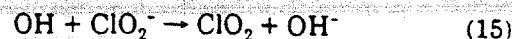
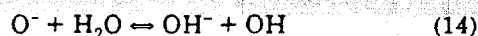
We propose the following overall stoichiometry for complete conversion of chlorite:



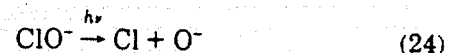
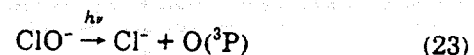
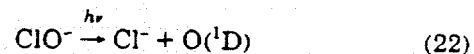
To explain the stoichiometry, we examine reaction steps which have been previously proposed. According to Buxton and Subhani (1972b), the primary photodecomposition of chlorite ion may occur in several ways:



followed by secondary reactions,



ClO^- is also decomposed by ultraviolet light as shown by Buxton and Subhani (1972a). They proposed



Our proposed stoichiometry can be explained by the addition of reactions 9, 18, 14, 15, and 22 (or 23), the sum of which equals reaction 21.

On the basis of our results we believe that reaction 9 is more likely to occur than reaction 8 since ClO would further react, yielding chlorate. Reaction 7 has been shown by Buxton and Subhani to be unimportant at 253.7 nm. Similarly we suspect that reactions 22 and 23 are faster than 24 since Cl would further react (in a complicated pattern involving chlorite), producing chlorate. It has also been shown by Karpel Vel Leitner *et al.* in another article (1991) that the reaction between hypochlorite and chlorite in basic solution produces chlorate. However, our results suggest that this reaction, like reactions 7, 8, and 24, is of lesser importance than the reactions we included in the mechanism.

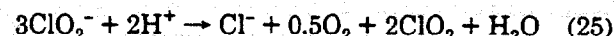
Our overall stoichiometry is supported by the overall photodecomposition reactions reported by Karpel Vel Leitner *et al.* (1992a). For the decomposition of chlorine dioxide they proposed the following reaction:



For the decomposition of chlorite, they proposed

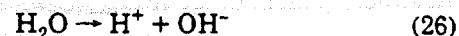


If we treat these two reactions as simultaneous algebraic equations, we eliminate chlorate by multiplying equation 19 by 3 and equation 6 by 2, and subtracting one equation from the other. The result of this calculation is



If we combine this equation with

001640



and eliminate H^+ , we obtain equation 21.

Assuming the proposed mechanism (reactions 9, 18, 14, 15, 22, or 23) for formation of chlorine dioxide and assuming chlorate forms from chlorine dioxide by reaction 6, we can estimate the distribution of chlorine dioxide, chloride, and hydroxide we might have observed in our experiments if chlorine dioxide had been completely sparged from the reactor before it reacted.

Table 5 (column 2) shows the experimental distribution. To eliminate chlorate from the products in Table 5, we use the stoichiometry of reaction 6. This reaction shows that the 4 mol of chlorate would be produced from 4/0.6 = 6.7 mol of chlorine dioxide. Therefore, if chlorate had not formed, the product distribution would contain an additional 6.7 mol of chlorine dioxide. Reaction 6 also predicts that the products would contain an additional $0.4 \times 6.7 = 2.7$ mol of chloride and would contain 6.7 mol less of hydroxide ions.

Table 5. Experimental Product Yields, Corrected Experimental Product Yields, and Theoretical Product Yields Based on Reaction 21, in the Case of Unbuffered Reactor Solutions

species	experitl product yields		theor product yields based on reaction 21
	unbuffered soln	corr for ClO ₂ decompn	
ClO ₂ ⁻ reacted	100	100	100
ClO ₂	60 ± 3	67	66.7
Cl ⁻	30 ± 4	32	33.3
OH ⁻	71 ± 5	64	66.7
Cl ₂	2 ± 2		
ClO ⁻	5 ± 0.5		
ClO ₃ ⁻	4 ± 0.5		

Table 6. Quantum Yield of Photodecomposition of Sodium Chlorite and Quantum Yield of Production of Chlorine Dioxide at 254 nm, for Various pH Conditions

pH	product	average rate (M/min) × 10 ³	quantum yield
unbuffered	ClO ₂ produced	0.583	0.47
	ClO ₂ ⁻ reacted	0.967	0.77
4	ClO ₂ produced	1.000	0.80
	ClO ₂ ⁻ reacted	1.556	1.24
5	ClO ₂ produced	1.149	0.92
	ClO ₂ ⁻ reacted	1.789	1.43
6	ClO ₂ produced	1.176	0.94
	ClO ₂ ⁻ reacted	1.922	1.53
7	ClO ₂ produced	0.839	0.67
	ClO ₂ ⁻ reacted	1.482	1.18
8	ClO ₂ produced	0.674	0.54
	ClO ₂ ⁻ reacted	1.148	0.92
9	ClO ₂ produced	0.586	0.47
	ClO ₂ ⁻ reacted	0.948	0.76
10	ClO ₂ produced	0.543	0.43
	ClO ₂ ⁻ reacted	0.900	0.72

To eliminate the 5 mol of hypochlorite from the products in Table 5, we assume that hypochlorite would eventually react by reaction 22 or 23, producing 5 mol of chloride. Therefore, this 5 mol would be added to the product distribution. We did not attempt to account for the chlorine which we found in the absorber samples, because of the large uncertainty associated with its concentration and the large percentage deviation we observed in repeated experiments.

The sums of all of the adjustments to the product distribution are -4 mol of chlorate, -5 mol of hypochlorite, +6.7 mol of chlorine dioxide, +7.7 mol of chloride, and -6.7 mol of hydroxide. Table 5 gives a comparison between experimental coefficients, corrected experimental coefficients, and theoretical stoichiometric coefficients based on reaction 21.

Table 7. Irradiation of Sodium Chlorite. Effect of Nitrogen Flow Rate on Rates of Production and Product Yields. Twelve Lamps in Use. Unbuffered Reactor Solutions

species	nitrogen flow rate (cm ³ /min)						
	0	500	1000	2000	3000	4000	5000
Rate of Production (M/min) × 10 ³							
ClO ₂ ⁻ reacted	0.61	0.70	0.77	0.81	0.87	0.97	0.95
ClO ₂	0	0.14	0.26	0.41	0.48	0.58	0.57
Cl ⁻	0.26	0.29	0.32	0.25	0.27	0.29	0.28
OH ⁻	NM ^a	0.29	0.43	0.53	0.60	0.69	0.70
Cl ₂	NM	0.06	0.06	0.04	0.03	0.02	0.02
ClO ₃ ⁻ and ClO ⁻	0.29 and 0.06	0.15	0.17	0.06	0.06	0.04 and 0.05	0.06
Product Yield (M/M of Chlorite Reacted)							
ClO ₂ ⁻ reacted	100	100	100	100	100	100	100
ClO ₂	0	20	33	51	55	60	60
Cl ⁻	43	42	42	32	32	29	30
OH ⁻	NM	41	56	66	69	71	74
Cl ₂	NM	8	8	5	3	2	2
ClO ₃ ⁻ and ClO ⁻	48 and 10	22	9	7	7	4 and 5	

^a NM = not measured.

D. Quantum Yield of Sodium Chlorite Photodecomposition and Chlorine Dioxide Production. To determine the quantum yield of sodium chlorite decomposition, we divided the rate of decomposition of sodium chlorite by the absorbed photon flux determined earlier. Sodium chlorite decomposition experiments were run with a reactor configuration utilizing 12 lamps. The absorbed photon flux is in that case 1.4606×10^{-6} mol of photon/s.

Table 6 shows the quantum yield of photodecomposition of chlorite and the quantum yield of production of chlorine dioxide for various pH values. These results are in very good agreement with the study of Karpel Vel Leitner *et al.* (1992b). They found a quantum yield of photodecomposition of sodium chlorite equal to 1 for a pH between 7 and 8. We found a value of 1.18 at pH 7 and 0.92 at pH 8. Our results are also in good agreement with the results given by Buxton and Subhani (1972b). At 253.7 nm they found a quantum yield of chlorite decomposition equal to 0.54 at pH 10 and 0.9 at natural pH. For the quantum yield of chlorine dioxide production, they determined a value of 0.24 at pH 10 and 0.41 at natural pH.

E. Effect of Nitrogen Flow Rate on the Reaction. The effect of the nitrogen flow rate used in sparging product gases from solution, has been investigated using the reactor equipped with 12 lamps and unbuffered chlorite solution with a concentration of 0.095 M. Flow rates ranged between 0 and 5000 cm³/min.

Table 7 shows the rates of production and product yields for several values of nitrogen flow rate. The table shows that, at zero flow rate, no chlorine dioxide is observed after a sufficient time of irradiation. As flow rate increases, chlorine dioxide and hydroxide increase while chloride and chlorate plus hypochlorite decrease substantially. These results are consistent with previous discussion and show that at low flow rates our results suggest the stoichiometry observed by Karpel Vel Leitner *et al.* (1992a). At high flow rate (as chlorine dioxide is more rapidly removed) the stoichiometry approaches that of reaction 21.

The sparging rate plays an important part in the production of chlorine dioxide. If it is too low, chlorine dioxide is decomposed due to a large residence time in the reactor. The decomposition of chlorine dioxide absorbs part of the ultraviolet light which is therefore not available for the decomposition of chlorite. This would explain the decrease in the rate of decomposition of chlorite at low nitrogen flow rate. If the flow rate is too high, some of the reactor solution might be removed by entrainment.

F. Effect of Initial Sodium Chlorite Concentration. The effect of initial chlorite concentration was investigated

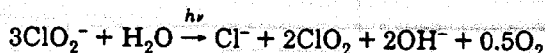
001641

using unbuffered sodium chlorite solutions and the photochemical reactor equipped with 12 lamps. The nitrogen flow rate was held constant at 4000 cm³/min. The initial concentrations used were 0.01, 0.04, and 0.09 M. Product yields were not affected by the change in the initial concentration. At the conditions of this study, the initial concentration does seem to have a significant effect on rates of production and rate of chlorite photodecomposition.

Conclusions

In studies of photodecomposition of chlorine dioxide by irradiation with ultraviolet light, we determined the quantum yield of photodecomposition of chlorine dioxide at 253.7 and 300 nm. At 300 nm our results agreed with the value 1.4 given in the literature (Zika *et al.*, 1984). At 253.7 nm we determined a quantum yield of photodecomposition equal to 0.44 at 25 °C.

In studies of the reaction of photodecomposition of sodium chlorite in aqueous solution with rapid removal of chlorine dioxide by sparging with nitrogen, we showed chloride and chlorine dioxide to be the major products of the photodecomposition. We propose the following overall reaction:



On the basis of our work and the work of several authors, we conclude that chlorate is not formed directly as a product of the photodecomposition of chlorite, but by decomposition of chlorine dioxide produced from chlorite. Although some hypochlorite may be formed as an intermediate, it is also further decomposed to chloride and oxygen.

At natural pH, we found a quantum yield of chlorite decomposition equal to 0.77 and a quantum yield of chlorine dioxide production equal to 0.47. These values are in good agreement with those found in the literature (Buxton and Subhani, 1972b).

The rate of photodecomposition of chlorite increases with decreasing pH. Product yields remained constant for all values of pH.

Acknowledgment

We gratefully acknowledge Eka Nobel, Inc., for financial support of this work. We thank Dr. M. Fazlul Hoq for technical assistance, especially in establishing analytical procedures and chemical purification methods, and Dr. Laren Tolbert for use of the photochemical chamber and for helpful discussions and advice.

Nomenclature

(ClO₂)^{*} = chlorite ion in excited state
O(¹D) = oxygen atom in excited state
O(³P) = oxygen atom in ground state
hν = photon

Literature Cited

Aieta, E. M.; Roberts, P. V.; Hernandez, M. Determination of Chlorine, Chlorite, and Chlorate in Water. *J. Am. Water Works Assoc.* 1984, 76 (1), 64.

- Bowen, E. J.; Cheung, W. M. The Photodecomposition of Chlorine Dioxide Solution. *Proc. Chem. Soc.* 1932, 1200.
- Buxton, G. V.; Subhani, M. S. Radiation Chemistry and Photochemistry of Oxychlorine Ions. Part 2.—Photodecomposition of Aqueous Solutions of Hypochlorite Ions. *J. Chem. Soc., Faraday Trans. 1* 1972a, 68, 958.
- Buxton, G. V.; Subhani, M. S. Radiation Chemistry and Photochemistry of Oxychlorine Ions. Part 3.—Photodecomposition of Aqueous Solutions of Chlorite Ions. *J. Chem. Soc., Faraday Trans. 1* 1972b, 68, 970.
- Callera, J. Process for the Production of Chlorine Dioxide. US Pat. 4,874,489, 1989.
- Calvert, J. G.; Pitts Jr., J. N. *Photochemistry*; John Wiley & Sons Inc.: New York, NY, 1967; p 748.
- Day, G. A.; Fenn, E. F. Process for Producing Chlorine Dioxide. US Pat. 2,484,402, 1949.
- Engström, J.; Norell, M. Process for the Production of Chlorine Dioxide. US Patent No. 5091166, Feb 25, 1992.
- Engström, J.; Falgén, H. Process for the Production of Chlorine Dioxide. US Patent No. 5091167, Feb 25, 1992.
- Fisher, R. P. Method for Generating Chlorine Dioxide Gas. US Pat. 4,414,180, 1983.
- Fisher, R. P. Photochemical Method for Generating Chlorine Dioxide Gas. US Pat. 4,456,411, 1984.
- Hatchard, C. G.; Parker, C. A. A New Sensitive Chemical Actinometer. II. Potassium Ferrioxalate as a Standard Chemical Actinometer. *Proc. R. Soc.* 1956, 253A, 518.
- Holst, T. G. Processes for Producing Chlorine Dioxide. US Pat. 2,373,830, 1945.
- Karpel Vel Leitner, N.; De Laat, J.; Doré, M.; Suty, H. Kinetics of the Reaction Between Chlorine and Chlorite in Dilute Aqueous Solution. *Environ. Technol.* 1991, 12, 477.
- Karpel Vel Leitner, N.; De Laat, J.; Doré, M. Photodecomposition of Chlorine Dioxide and Chlorite by U.V.-irradiation-Part I. Photoproducts. *Water Res.* 1992a, 26, 1655.
- Karpel Vel Leitner, N.; De Laat, J.; Doré, M. Photodecomposition of Chlorine Dioxide and Chlorite by U.V.-irradiation-Part II. Kinetic Study. *Water Res.* 1992b, 26, 1665.
- Koller, L. R. *Ultraviolet Radiation*; John Wiley & Sons Inc.: New York, NY, 1952; pp 140-150.
- Masschelein, W. J. *Chlorine Dioxide*; Ann Arbor Science Publications: Ann Arbor, MI, 1979.
- Peintler, G.; Nagypal, I. Kinetics and Mechanism of the Reaction Between Chlorite Ion and Hypochlorous Acid. *J. Phys. Chem.* 1990, 94, 2954.
- Persson, S. H. Chlorine Dioxide Manufacture. US Pat. 2,376,935, 1945.
- Rand, M. C.; Greenberg, A. E.; Taras, M. J. Eds. *Standards Methods for the Examination of Water and Wastewater*, 14th ed.; American Public Health Association: Washington, DC, 1975; pp 273 and 306.
- Rapson, W. H. The Mechanism of Formation of Chlorine Dioxide from Sodium Chlorate. *TAPPI* 1956, 39, 554.
- Rapson, W. H. Recent Developments in the Manufacture of Chlorine Dioxide. *Can. J. Chem. Eng.* 1958, 36, 262.
- Rapson, W. H.; Wayman, M. Method for Removing Chlorine from Mixtures Containing Chlorine Dioxide and Chlorine. US Pat. 2,481,241, 1949.
- Rapson, W. H.; Wayman, M. A Continuous Process for the Manufacture of Chlorine Dioxide. *Pulp Pap. Mag. Can.* 1954, 55 (6), 92.
- Rosen, H. J. Method of Simultaneously Producing Chlorine Dioxide and a Sulfate Salt. US Pat. 3,933,988, 1976.
- Sekisui Plastics Co. Ltd. Preparing Chlorine Dioxide by Irradiating UV on Chlorite Aqueous Solution. *Jap. Pat.* 091375, 1991.
- Zika, R. G.; Moore, C. A.; Gidel, L. T.; Cooper, W. J. Sunlight-induced Photodecomposition of Chlorine Dioxide. *Water Chlorination: Chem. Environ. Impact Health Eff., Proc. Conf.* 1984, 5th, 1041.

Received for review July 26, 1993

Revised manuscript received February 22, 1994

Accepted March 7, 1994*

* Abstract published in *Advance ACS Abstracts*, April 15, 1994.

001642



of ammonium salts can be utilized for activating chlorite solutions.

References

1. WHITE, J. F., TAYLOR, M. C. & VINCENT, G. P., *Industr. Engng Chem.*, **34** (1942), 782.
2. TAYLOR, M. C., WHITE, J. F., VINCENT, G. P. & CUNNINGHAM, G. L., *Industr. Engng Chem.*, **32** (1940), 899.
3. *Brit. Pat.* 561,229 (to Mathieson Alkali Works), 1942.
4. TAYLOR, M. C., WHITE, J. F. & VINCENT, G. P., *Chem. Abstr.*, **35** (1941), 6449.
5. SKELLY, J. K., *J. Soc. Dy. Col.*, **76** (1960), 469.
6. HEFTI, H., *Text. Res. (J.)*, **30** (1960), 861, 867.
7. WHITE, J. F., *Amer. Dyest. Rep.*, **31** (1942), 484.
8. BRITTON, H. T. S., *Hydrogen ions*, Vol. I (Chapman & Hall Ltd. London), 1955, 319-51.
9. EARLAND, C. & JOHNSON, K. G., *Text. Res. (J.)*, **22** (1952), 591.
10. FINDLAY, A., *Introduction to physical chemistry* (Longmans, Green & Co., London), 1942, 326-49.
11. MELLOR, J. W., *A comprehensive treatise on inorganic and theoretical chemistry*, Vol. II (Longmans, Green & Co., London), 1922, 282.

EN



Studies in Sodium Chlorite: Part II—The Mechanism of Photodecomposition of Sodium Chlorite

G. M. NABAR, C. R. RAMACHANDRAN & V. A. SHENAI

Department of Chemical Technology, University of Bombay, Bombay 19

Manuscript received 3 May 1963

The photodecomposition of aqueous sodium chlorite solutions at different pH values has been investigated using sunlight and light emitted by an enclosed carbon arc. The extent of decomposition has been found to fall with increase in pH and the initial concentration of the solution. The presence of soluble chloride has no influence on the extent of photodecomposition. Based on the analysis of photodecomposition products at different pH values, mechanisms I and II have been proposed for the decomposition of acidic and alkaline solutions respectively:



AQUEOUS sodium chlorite solutions, which are stable under alkaline conditions, can be activated by acidification. Activated chlorite solutions evolve chlorine dioxide and find use in the bleaching of textiles and wood pulp. In an earlier communication¹, it has been shown that under certain conditions ammonium salts activate sodium chlorite solutions. Incident light is also known to activate chlorite solutions with the liberation of chlorine dioxide.

No work seems to have been done on the stoichiometry of photodecomposition of sodium chlorite. A systematic quantitative investigation of the products of photodecomposition of aqueous sodium chlorite solutions, at acidic and alkaline pH values, was, therefore, undertaken. Based on the results of these investigations, a mechanism for the photodecomposition of sodium chlorite has been proposed.

Experimental Procedure

Commercial sodium chlorite of the following composition was used: NaClO₂, 78.10; NaClO₃, 1.30; NaCl, 15.31; and moisture, 2.68 per cent. A 0.1 per cent solution of sodium chlorite had a pH of 9.30.

In the study of the chemistry of photodecomposition of chlorite, the total available chlorine, chlorine dioxide, total oxidizing power and chloride were estimated by standard methods^{2,3}.

Photodecomposition of chlorite solutions—For the study of the effect of light on the nature of

decomposition, light emitted by an enclosed carbon arc of Atlas fadeometer was used. In some experiments, sunlight was also used; these experiments were carried out at about the same time every day and as far as possible completed within a week so as to minimize any variation due to possible changes in the spectral energy distribution caused by meteorological and geographical factors. Buffered chlorite solutions were exposed in pyrex test tubes fixed to the rotating frame of the fadeometer.

The photodecomposition of sodium chlorite was studied under various conditions of pH, concentration and period of exposure.

Results and Discussion

001643

Effect of pH on the self-decomposition of sodium chlorite—In order to study the effect of change in pH on the self-decomposition of sodium chlorite in the dark, 0.1N solutions were adjusted to various pH values at room temperature and stored in the dark for 3 hr. The chlorite content was estimated in the beginning and also at the end of 3 hr. The extent of decomposition at pH 4.0, 4.9, 6.0, 7.4 and 7.98 was 2.5, 1.5, 1.1, 0.6 and 0.4 per cent respectively. These results indicate that there is slight decomposition of chlorite under these conditions and the percentage decomposition decreases with increase in pH. In the case of exposure of unbuffered chlorite solutions to light, with increase in the period of exposure, the pH of the solution showed a small rise initially followed by a slight but progressive decrease (Fig. 1). Similar

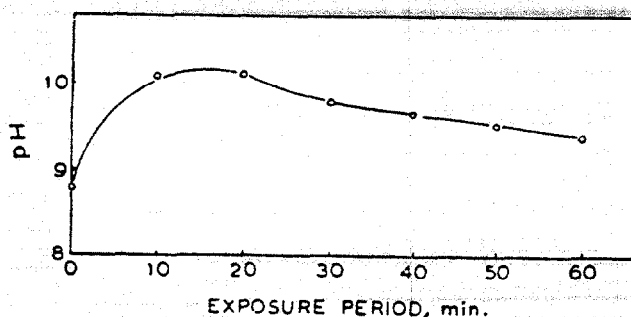


Fig. 1 — Effect of period of exposure in fadeometer on the pH of sodium chlorite solution

observations have been recorded for thermal decomposition of sodium chlorite⁴.

To study the effect of pH on the photodecomposition of aqueous sodium chlorite, 0.1N solutions were buffered to various pH values and exposed to fadeometer arc for 30 min. The extent of decomposition of sodium chlorite solution buffered to pH 4.76 using sodium acetate+acetic acid buffer was 79.2 per cent. Solutions buffered with sodium dihydrogen phosphate+disodium hydrogen phosphate buffer to pH values 5.84, 6.94 and 8.94 showed decomposition of the order of 68.93, 67.38 and 48.70 per cent respectively. The activating influence of light on the decomposition of sodium chlorite is evident from these results. In this case also, as observed earlier, the percentage decomposition decreases with increase in pH. Thermal decomposition of sodium chlorite follows the same trend⁴.

Influence of chlorides on photodecomposition of sodium chlorite—Barnett⁵ found that chlorides accelerate the thermal decomposition of chlorites. White *et al.*⁶ reported that there was no acceleration of the decomposition of chlorite due to the presence of chlorides. In view of these contradictory reports, it was considered of interest to examine whether chlorides influence the photodecomposition of sodium chlorite. Different quantities of sodium chlorite were dissolved in 50 ml. each of aqueous sodium chlorite solution (0.085N) in pyrex test tubes and

exposed to fadeometer arc for 30 min. The extent of decomposition of sodium chlorite with 20, 60, 80, 100 and 120 g./litre sodium chloride added was 27.40, 27.89, 28.34, 28.78 and 28.87 per cent respectively as compared to 28.50 in the absence of sodium chloride. Contrary to the views expressed by Barnett⁵, these results indicate that sodium chloride does not accelerate the photodecomposition of sodium chlorite.

Rate of photodecomposition of sodium chlorite—Aqueous solutions of sodium chlorite, buffered to pH 8.2 and 3.8, were exposed to fadeometer arc in pyrex test tubes. The decomposition of sodium chlorite was determined every 10 min. The results given in Table 1 show that the percentage decomposition decreases with increase in the initial concentration, both in the alkaline and acidic pH ranges. However, when the decomposition is expressed in g./litre, high starting concentrations give higher decomposition values under alkaline as well as acidic conditions.

Relative photodecomposition of sodium chlorite solutions in fadeometer and in sunlight—An aqueous sodium chlorite solution (0.02N) was exposed separately to fadeometer arc light and to direct sunlight. The final concentration of sodium chlorite was determined in both cases. The average temperature of the solution was 54°C. in the fadeometer and 36°C. in sunlight. The results presented in Fig. 2 show that the decomposition behaviour of chlorite is similar in both the cases, but the extent of decomposition is different. This may be primarily due to the difference in the intensity and spectral distribution of the incident light as well as the difference in temperature in the two cases. Experiments carried out with different initial concentrations (0.05 and 0.0143N) of sodium chlorite gave similar results. However, in both types of exposure, the percentage decomposition increases with decrease in initial concentration in the concentration range studied.

Stoichiometry of photodecomposition of sodium chlorite—For an understanding of the mechanism of photodecomposition of sodium chlorite it is necessary to consider the stoichiometry of the

TABLE 1 — RATE OF PHOTODECOMPOSITION OF BUFFERED SODIUM CHLORITE SOLUTIONS

pH	Initial conc. of NaClO ₂ N	Decomposition (%) of sodium chlorite after						
		10 min.	20 min.	30 min.	40 min.	50 min.	60 min.	80 min.
8.20	0.0409	24.84 (0.23)*	58.17 (0.54)	83.66 (0.77)	85.23 (0.79)	96.07 (0.89)	98.04 (0.91)	—
	0.0878	8.51 (0.17)	30.09 (0.60)	55.01 (1.09)	81.17 (1.61)	—	96.99 (1.93)	98.79 (1.96)
	0.1020	4.97 (0.11)	21.99 (0.51)	46.86 (1.08)	72.27 (1.67)	—	91.35 (2.11)	98.72 (2.28)
	0.1549	—	—	—	—	—	—	—
3.80	0.0775	9.05 (0.159)	30.86 (0.542)	65.66 (1.152)	96.99 (1.702)	99.77 (1.752)	—	—
	0.1058	10.21 (0.244)	30.28 (0.725)	54.44 (1.303)	74.49 (1.783)	99.15 (2.368)	99.84 (2.370)	—
	0.1549	8.94 (0.314)	—	38.68 (1.356)	—	81.06 (2.842)	97.21 (3.408)	—
	0.2077	—	—	—	—	—	—	—

*The values given in parentheses represent sodium chlorite decomposed, g./litre of solution.

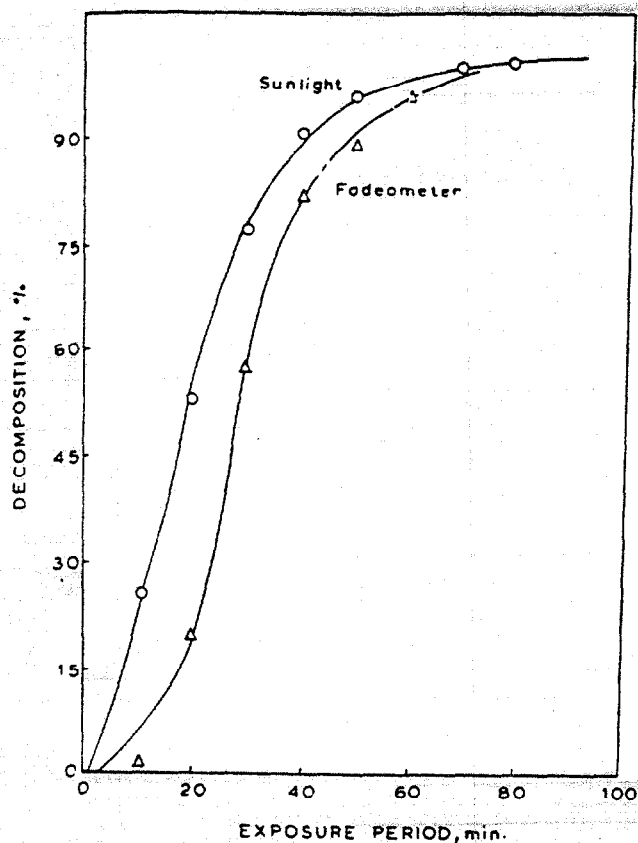


Fig. 2 — Effect of period of exposure to light on the decomposition of sodium chlorite

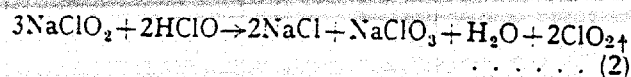
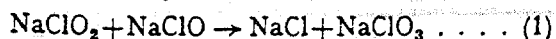
photoreaction. When sodium chlorite solution is exposed to light, sodium chlorate, sodium perchlorate, sodium hypochlorite, sodium chloride, chlorine dioxide and oxygen are likely to be formed. In addition to these, varying quantities of sodium chlorite may also be present depending on the degree of decomposition.

From preliminary experiments the following observations were made with regard to the nature of the products formed as a result of photodecomposition:

Sodium chlorite, being the major component of the starting material, was present in the final products, where decomposition had not proceeded to completion.

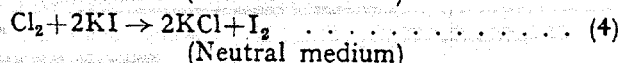
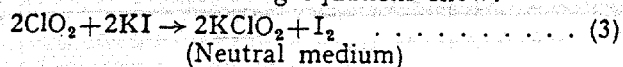
Sodium chloride and sodium chlorate were already present as impurities in the commercial sodium chlorite used. These were also formed due to the photodecomposition of sodium chlorite. Experiments conducted on chemically pure sodium chloride and sodium chlorate showed that these salts were not affected by light under the conditions of the experiment.

Sodium hypochlorite was not found either in the original chlorite or in the reaction products. At no stage of the reaction hypochlorite was found to be present. If hypochlorite is formed during the reaction as an intermediate product, it would get decomposed instantaneously. Since hypochlorite cannot exist in the presence of chlorite, they react with each other according to the following equations, depending on pH^8 :



Sodium perchlorate — An aqueous solution of sodium chlorite (5 per cent), approximately of pH 3-4, was exposed to light till the decomposition was complete, when the solution became colourless. It was then evaporated to dryness on a water-bath, cooled, extracted with 5 ml. of 5*N* hydrochloric acid and evaporated again till the evolution of gases subsided. The residue was dissolved in distilled water and neutralized⁷. Sodium perchlorate was found to be present in the reaction products. In some experiments, aqueous solutions of potassium perchlorate (Analar) were exposed to light for different periods. Perchlorate was not affected by the exposure.

*Chlorine dioxide and chlorine*³ — The gases formed during photodecomposition of sodium chlorite were absorbed in neutral potassium iodide solution. The liberated iodine was titrated against standard sodium thiosulphate solution. To another aliquot, dilute acetic acid was added and the iodine liberated estimated. The volume of thiosulphate solution for the first titration was one-fifth the volume of that for the second. This showed that only chlorine dioxide was formed and not chlorine. If chlorine were also formed, the ratio of volumes of thiosulphate solution in the two cases would have been different as the following equations show:



Analysis of reaction products — Preliminary experiments showed that pH is of considerable importance in the study of the chemistry of chlorites. Hence, the proportions of the products formed under varying conditions of pH were determined with a view to arriving at a reaction mechanism which would explain the photodecomposition of sodium chlorite.

Unbuffered aqueous solutions of sodium chlorite (50 ml.) were exposed to fadeometer arc for 2 hr and sodium chlorite, chlorate and chloride were estimated in the reaction products by the methods already mentioned. From the results given in Table 2, it is obvious that the quantity of sodium chlorite decomposed and the amounts of sodium chlorate and chloride formed can be expressed as:

0.1853 g. $NaClO_2$ on decomposition gives 0.0810 g. $NaClO_3$ and 0.0795 g. $NaCl$ (Exp. I)

0.2005 g. $NaClO_2$ on decomposition gives 0.0887 g. $NaClO_3$ and 0.0877 g. $NaCl$ (Exp. II)

0.0500 g. $NaClO_2$ on decomposition gives 0.01942 g. $NaClO_3$ and 0.0222 g. $NaCl$ (Exp. III)

Expressing these results in terms of moles,

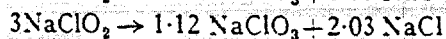
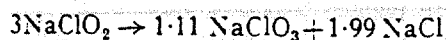
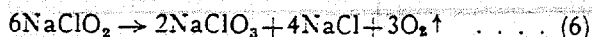


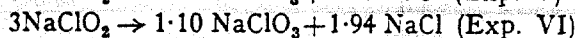
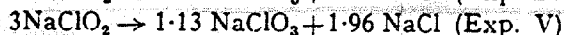
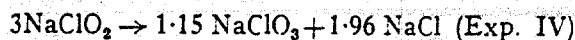
TABLE 2 — ANALYSIS OF PRODUCTS FORMED BY EXPOSING UNBUFFERED AQUEOUS SOLUTIONS OF SODIUM CHLORITE FOR VARIOUS PERIODS

Product	0.1816N soln			0.045N soln	
	Initial amount g.	Amount after 1 hr (Exp. I)	Amount after 2 hr (Exp. II)	Initial amount g.	Amount after 2 hr (Exp. III)
Sodium chlorite	0.2055	0.0202	0.0050	0.0509	0.0008
Sodium chlorate	0.0073	0.0883	0.0956	0.0011	0.0205
Sodium chloride	0.0392	0.1187	0.1269	0.0129	0.0351

By rounding off, the photodecomposition of an unbuffered sodium chlorite solution may be represented as follows:

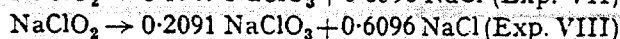


From the results of analysis of the decomposition products obtained by exposing sodium chlorite solutions, buffered to pH 8.43, the following observations were made:



i.e. $6\text{NaClO}_2 \rightarrow 2\text{NaClO}_3 + 4\text{NaCl}$ and, therefore, the reaction carried out at pH 8.43 can also be represented by Eq. (6). The production of oxygen as a result of the decomposition of sodium chlorite has been reported^{8,9}. Under alkaline conditions sodium chlorite appears to decompose quantitatively into sodium chlorate, sodium chloride and oxygen.

On exposing aqueous sodium chlorite solutions buffered to pH 4.0 the following observations were made:

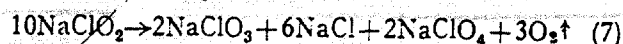


The mode of photoreaction of sodium chlorite under acidic conditions appears to be different from that under alkaline conditions. Acidic solutions decompose both due to acidification and photo-activation. However, photodecomposition is the predominant reaction as could be seen from the fact that a 0.1N solution of sodium chlorite at pH 4 decomposed to the extent of only 2.5 per cent at room temperature in 3 hr in the dark (Table 1), whereas the same, when exposed to fadeometer arc, decomposed almost completely in c. 1 hr. The chlorate and chloride formed did not account for all the sodium and chlorine present in the sodium chlorite decomposed. For every molecule of sodium chlorite decomposed, 0.2 atom of sodium and 0.2 atom of chlorine could not be accounted for by chlorate and chloride formed.

As mentioned earlier, qualitative examination of the photodecomposition products of sodium chlorite showed the presence of chlorate, chloride and

perchlorate. Since chlorate and chloride account for 80 per cent of the total sodium (in terms of atoms), it is probable that the balance of 20 per cent sodium is present as sodium perchlorate.

Hence, the photodecomposition under acidic conditions may be represented as:



The results of the foregoing may be summarized as follows:

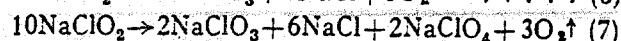
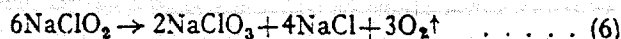
1. During photodecomposition of aqueous sodium chlorite solution, the pH of the solution increases in the initial stages of exposure, followed by a slow decrease.

2. In both the cases of exposure, i.e. to sunlight and carbon arc, the percentage decomposition of sodium chlorite decreases with increase in pH of the solution.

3. Soluble chlorides neither accelerate nor retard the photodecomposition of sodium chlorite.

4. The percentage decomposition of sodium chlorite during exposure to light decreases with increasing starting concentration.

5. By analysing the reaction products quantitatively, the following chemical equations for the photodecomposition of sodium chlorite solutions, under alkaline and acidic conditions respectively, are suggested:



References

1. NABAR, G. M., SHENAI, V. A. & SUNDARAM, S., *Indian J. Technol.*, **2** (1964), 7.
2. WHITE, J. F., *Amer. Dyest. Rep.*, **31** (1942), 484.
3. OTHMER, K., *Encyclopedia of chemical technology*, Vol. 3 (Interscience Publishers Inc., New York), 1949, 703.
4. SUNDARAM, S., *Bleaching with sodium chlorite*, M.Sc. (Tech.) Thesis, University of Bombay, 1954.
5. BARNETT, B. cited in White, J. F., Taylor, M. C. & Vincent, G. P., *Industr. Engng Chem.*, **34** (1942), 782.
6. WHITE, J. F., TAYLOR, M. C. & VINCENT, G. P., *Industr. Engng Chem.*, **34** (1942), 782.
7. NABAR, G. M. & RAMACHANDRAN, C. R., *Analyt. Chem.*, **31** (1959), 263.
8. TAYLOR, M. C., WHITE, J. F., VINCENT, G. P. & CUNNINGHAM, G. L., *Industr. Engng Chem.*, **32** (1940), 899.
9. LEVI, G. R., *C.R. Accad. Lincei*, **31** (1922), 370.

001646



EN



WATER CHLORINATION

**Chemistry,
Environmental Impact
and Health Effects**

Volume 5

Edited by

**Robert L. Jolley
Richard J. Bull
William P. Davis
Sidney Katz
Morris H. Roberts, Jr.
Vivian A. Jacobs**

**Proceedings of the Fifth Conference on
Water Chlorination: Environmental Impact and Health Effects
Williamsburg, Virginia
June 3-8, 1984**

**Sponsored by
Electric Power Research Institute, National Cancer Institute,
Oak Ridge National Laboratory, Tennessee Valley Authority,
U.S. Department of Energy, U.S. Environmental Protection Agency,
Virginia Institute of Marine Science-School of Marine Science, and
College of William and Mary**



LEWIS PUBLISHERS, INC.

001647

TD
4105
1130
1130



CHAPTER 82

Sunlight-Induced Photodecomposition of Chlorine Dioxide

Rod G. Zika, Cynthia A. Moore, Louis T. Gidel,
and William J. Cooper

Many water treatment facilities, at some point after or immediately before addition of the oxidant, expose the water being treated to direct sunlight. Because of the significant sunlight absorption by some of the oxidants, the chemical pathway leading to their decomposition can be dramatically altered. Potentially, this can have a pronounced effect on the nature of the inorganic by-products of the oxidant decomposition and on the halogenated organic materials produced via interaction with the oxidant photoproducts. In sunlight, direct photolytic decomposition will only be significant for those oxidants that exhibit appreciable light absorption at wavelengths longer than 300 nm. Of all the water treatment oxidants, ClO_2 is most prone to photochemical decomposition during sunlight exposure. This is because of its high light absorption in the near UV and visible region of the spectrum and high quantum yields, reported to be 1.0 mol/Einstein at 405 nm and lower wavelengths.

The gas-phase photochemistry of ClO_2 has been studied extensively.¹⁻⁴ However, far less attention has been paid to its photolysis in aqueous solution.⁵⁻⁸ In the gas phase, the primary photochemical reaction is the homolytic fission of the chlorine oxygen bond:

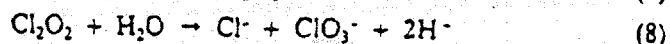
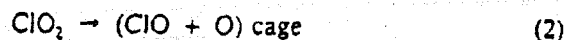


The products of this primary reaction then go on to generate secondary products such as chlorine peroxide (ClOO), excited state oxygen (O_2^*), chlorine (Cl_2), chlorine trioxide (Cl_2O_3), chlorine hexoxide (Cl_2O_6), and the recently proposed chlorine perchlorate (ClOClO_3).⁹

In aqueous solution, the primary photoreaction product ClO is not observed, and O appears to be a minor product since little O_3 is found in oxygenated aqueous solutions.⁸ It is postulated that the reaction proceeds, as in the gas phase, to give ClO and O , but these products then undergo solvent cage recombination to generate chlorine atoms and molecular oxygen. In addition, a rapid bulk solution reaction between ClO and ClO_2 produces Cl_2O_3 , and the reaction between Cl (or Cl_2^-) and ClO_2 leads to Cl_2O_3 . Rapid hydrolysis of Cl_2O_3 and Cl_2O_6 leads to the formation of the observed products ClO_3^- , ClO_2^- , and Cl^- . The overall reaction is as follows:

1041

001648



Interestingly, although ClO_2 has the distinct advantage in water treatment of not having the capacity to oxidize Br^- , many of its transient photolysis products do. The appearance of transitory species during the flash photolysis of ClO_2 solutions, which contained low levels of Br^- , have been reported.⁸ The transients are believed to be Br_2^- or BrCl^- . The information on the reactions of these radicals with organic compounds is scarce; however, it has been shown that they do react at appreciable rates with alcohols.⁹ By analogy with the Cl_2^- radical, bromine radical anions should undergo addition to alkenes and aromatic compounds.

In this chapter, the light-induced decomposition of ClO_2 is examined in an attempt to characterize inorganic products and trihalomethane (THM) formation, and to describe the extent to which sunlight-induced photodecomposition might occur during water treatment.

EXPERIMENTAL

Chlorine dioxide used in this study was prepared from sodium chlorite (80% purity) obtained from Alfa Products and potassium persulfate (reagent grade) obtained from Mallinckrodt. A standard procedure was used to prepare and handle the ClO_2 .¹⁰ Stock solutions thus prepared were stored refrigerated and protected from light. They were standardized immediately before being used in experiments.

Chlorine dioxide solutions for sunlight reaction studies were prepared by adding the concentrated stock solution to organic-demand-free water in 10-cm quartz spectrophotometer cells. The cells were sealed so that no headspace existed. The initial concentration was calculated from the measured absorbance at 360 nm using a molar extinction coefficient, Σ , of $1035 \text{ L mol}^{-1} \text{ cm}^{-1}$. Sunlight exposure experiments were conducted on the roof of the laboratory. The integrated solar flux during the experiments was determined with an Eppley Laboratory Ultraviolet Radiometer, Model TUVR. Changes in the ClO_2 and light absorbing product concentrations during the course of the experiments were determined from the UV-vis spectra. Controls were run

001649

simultaneously by storing sample cells in the dark at the same temperature as the light-exposed samples. Experiments involving fluorescent room lighting were conducted in a similar manner. The samples were exposed to standard laboratory fluorescent lights on a bench ~7 ft below overhead light fixtures.

Quantum yield studies were conducted using a Kratos/Schoeffel 1000-W mercury-xenon monochromatic irradiation system. Quantum yields were determined at the mercury lines 296.7, 313.0, 334.1, 366, 404.5, and 435.8 nm, with a bandwidth of ~7 nm. The intensity at each line was determined using ferrioxalate actinometry.¹¹ The measurements were performed in 10-cm quartz spectrophotometry cells in the same way as described for the sunlight experiments. Time intervals for light exposure varied (i.e., 10 to 120 s) and were optimized to examine the reaction during the first 10% of the decay curve.

Natural water samples were placed in 60-mL reaction vials, spiked with ClO_2 at $\sim 1.5 \times 10^{-4} \text{ M}$ (10 mg/L), topped with additional water, and capped with Teflon-lined septa. The vials were then either placed in the dark as controls or exposed to sunlight on the roof. The sunlight was monitored with the Eppley Radiometer, and the samples were exposed for a period in excess of twice the half-life for ClO_2 (a product of ClO_2 photodecomposition) photolysis. This interval was usually about 4 h at midday. The dark- and light-exposed samples were then quenched by adding a slight excess of sodium thiosulfate. The capped samples were refrigerated and analyzed by gas chromatography for THMs.¹² Samples for anion analysis were prepared by purging residual ClO_2 with N_2 gas to quench the reaction. Analyses were conducted using ion chromatography on a Dionex Model 10 chromatograph with a "fast anion" column and 0.0015 M Na_2CO_3 as eluant. The column flow rate was 3.0 mL/min. With these conditions, the approximate retention times in minutes for anions were ClO_2^- at 2.40; BrO_3^- at 3.10; Cl^- at 3.45; Br^- at 8.10; and ClO_3^- at 9.25.

RESULTS AND DISCUSSION

Sunlight Studies

001650

Aqueous solutions of ClO_2 in sealed 10-cm spectrophotometer cells were exposed to summer midday solar radiation. The resultant photochemical decay of ClO_2 is shown in Figure 1. The results indicate that ClO_2 should have a lifetime of <0.5 min in water exposed to bright sunlight. To evaluate the wavelength dependence of the reaction, quantum yields for the decomposition of ClO_2 were measured at various wavelengths. The quantum yields were compared with those determined earlier (Table I) by Bowen and Cheung.⁵ The reasons for the differences in quantum yields determined in the two studies are not apparent but could be the result of the differences in methodologies. There is, for instance, no information in the Bowen and Cheung report on the pH of the reaction solutions. Although differences between pH 7.0 and 9.0 appear to be negligible, it is possible that the spread could be significantly larger at more-

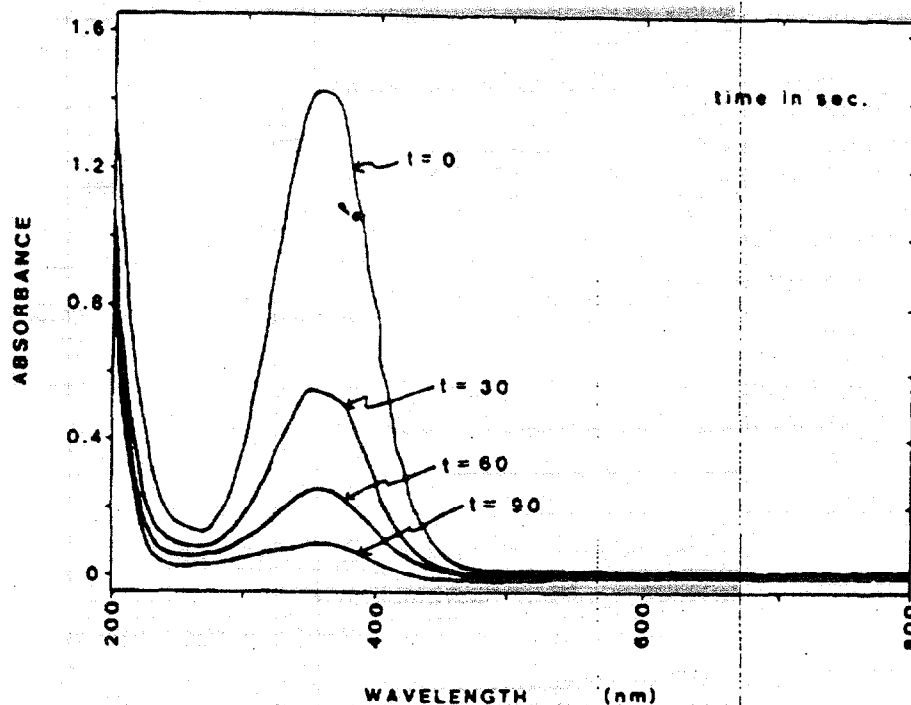


Figure 1. Photochemical decomposition of chlorine dioxide aqueous solution in sunlight.

Table I. Decomposition Quantum Yields (Φ) of ClO_2

Wavelength (nm)	From Bowen and Cheung ¹	This Work at pH	
		7.0	9.0
296.7		1.40 \pm 0.03	1.47 \pm 0.09
300	1.00		
313.0		0.98 \pm 0.02	0.86 \pm 0.01
334.1		0.90 \pm 0.02	0.90 \pm 0.02
366.0	0.76	0.46 \pm 0.02	0.46 \pm 0.02
404.5	0.51	0.13 \pm 0.02	
435.8	0.21		

acidic pH values. In water treatment applications, however, pH values in the 7 to 9 range are more likely to be encountered in ClO_2 treatment applications.

Another complication in comparing the results is caused by the possible differences in the bandwidth of the incident radiation. In the work presented here, a high-energy monochromator with a bandwidth of less than 7 nm was used to isolate mercury lines. It is clear from the Bowen and Cheung report

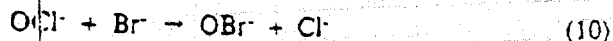
001651

that for the 300-nm value of $\Phi = 1.00$, a broad spectral region of 316 to 270 nm was used. The rapidly changing values of Φ and ClO_2 absorbance in this region make it unlikely that the quantum yields from the two studies would agree closely. This same problem could contribute to the lack of agreement at other wavelengths. Unfortunately, the filter combinations used in the Bowen and Cheung report to isolate other mercury lines could not be reproduced in our laboratory because the glass filters used are apparently no longer available.

Reaction Products

When ClO_2 is used as an oxidant in water treatment applications, the resultant thermal and photochemical decomposition pathways become considerably more complex than they are in pure water solutions of ClO_2 . Compositional variations in the particular water can have a pronounced effect on the mechanism and the products generated. The occurrence of oxidizable substrates in the water will contribute to the amount of ClO_2^- produced from ClO_2 via dark oxidation reactions. The photochemical decomposition of ClO_2 will then also involve ClO_2^- , which has a moderately strong electronic absorption spectra in the near-UV region of sunlight. The complex nature of the mechanism can be observed from the changing electronic absorption spectra of ClO_2^- solutions during sunlight exposure (Figure 2). It is obvious that ClO_2^- has a lifetime of < 10 min in full sunlight and that its reaction products are ClO_2 and OCl^- . The photochemistry of ClO_2^- has been extensively covered elsewhere^{13,14} and will not be further discussed here. It is worth noting, however, that the photochemistry of ClO_2 in disinfection application will to some extent, depending on the characteristics of the water and the light-spectral distribution, involve the oxidants ClO_2 , ClO_2^- and OCl^- .

The major stable end products of ClO_2 photolysis in aqueous solution are Cl^- , ClO_3^- and O_2 .⁵ The Cl^- and ClO_3^- are produced through hydrolysis of Cl_2O_3 and Cl_2O_2 , with ClO^- and Cl also involved in the reaction sequence.²⁻³ An advantage of ClO_2 in disinfection is its inability to oxidize Br^- ; however, in solution exposed to light, these intermediate oxidants could initiate reactions such as



In solutions of $1.5 \times 10^{-4} M$ ClO_2 , which were exposed to direct sunlight, ion chromatographic analysis revealed that the only major ionic products were Cl^- and ClO_3^- . When $1 \times 10^{-4} M$ Br^- was added to the solution, BrO_3^- was also observed as a product (Figure 3). Although the ClO_2 was photolyzed during the first few minutes of the reaction, the BrO_3^- gradually increased on contin-

001652

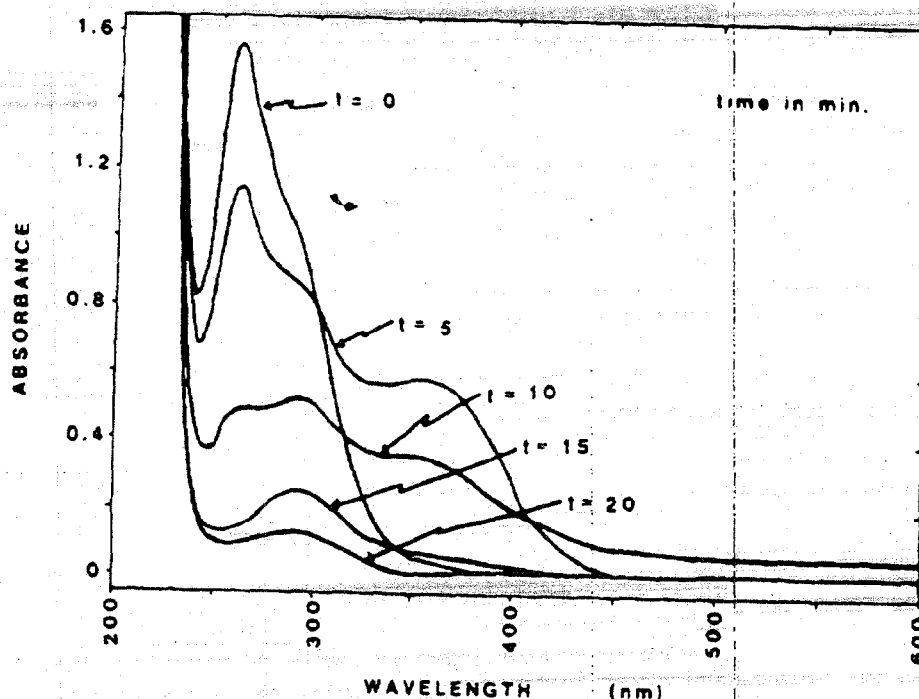
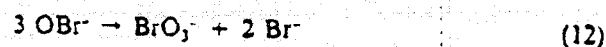


Figure 2. Photochemical decomposition of chlorite aqueous solution in sunlight.

001653

ued exposure to sunlight. The amount of Br^- concentration decreased initially to 50% of that added and then increased as the reaction proceeded. This is interpreted as an initial rapid oxidation of Br^- to OBr^- , which then reacts photochemically¹⁵



to generate the observed product distributions. The OBr^- would not be detected using the ion chromatographic determination as described previously.

In water containing significant amounts of labile organic materials, the organic product yields might vary because of available organic scavengers. When ClO_2 was added to groundwater and exposed to sunlight, THM analysis revealed a linear increase in bromoform formation with increasing Br^- concentration (Figure 4). The onset of significant CHBr_3 formation in this water appears at about 1 mg/L Br^- . A low yield of CHCl_3 was also observed which, within the limits of analytical precision, appeared to be independent of Br^- concentration.

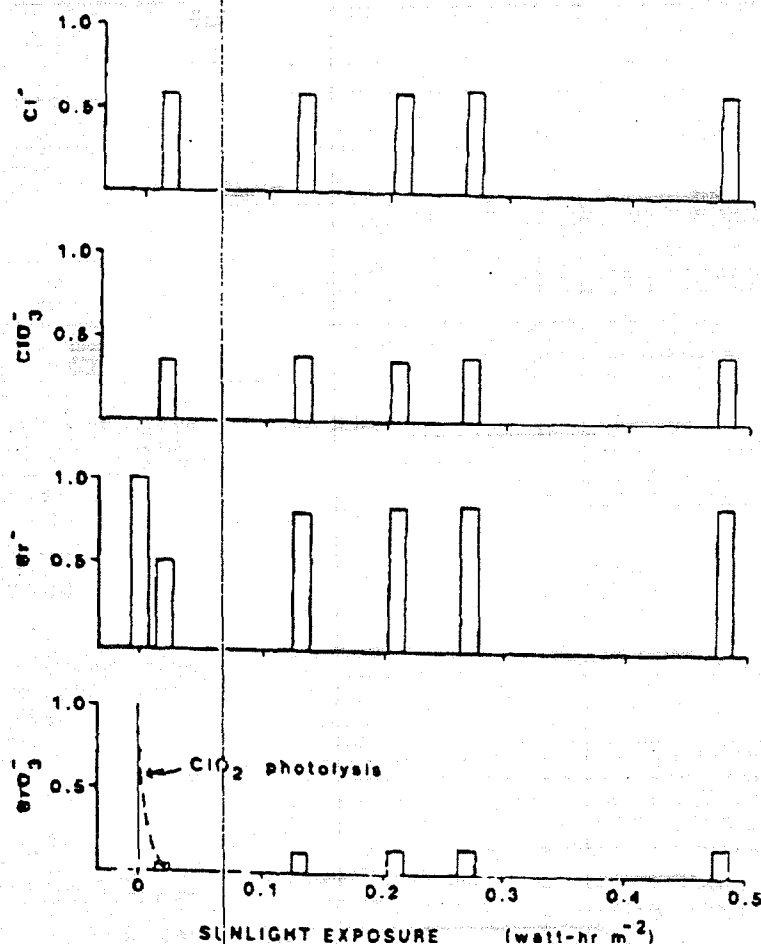


Figure 3. Major anionic products of ClO_2 photolysis in solutions containing $1 \times 10^{-4} \text{ M Br}^-$ and $1 \times 10^{-4} \text{ M ClO}_2$ at pH 7.0. Vertical axes represent relative molar concentration.

001654

To examine the effect of natural water composition on CHBr_3 formation, water from three different wells in the South Florida area was enriched with Br^- , dosed with $1.5 \times 10^{-4} \text{ M ClO}_2$, and exposed to sunlight. The yields of CHBr_3 are shown in Table II for pH 5, 7, and 9. The highest yields were observed for all water samples at pH 5, which is not consistent with the usual trend of increasing THM production with increasing pH. This decreasing yield could be due to an increased photolysis decomposition rate of the active bromine species at elevated pH.¹⁶ There is the added complication that water composition also affects the CHBr_3 production, as is indicated for the Orr well 2 sample, which displayed less pH dependence than the other two wellwater

Table II. Bromoform Formation from ClO_2 ($\mu\text{g/L}$)

Source of Water	pH 5		pH 7		pH 9	
	Light	Dark	Light	Dark	Light	Dark
Preston well 5	50	ND*	7	ND	0	ND
Orr well 2	44	ND	21	ND	17	
Northwest well 3	13	ND	ND	ND	ND	ND

*Not determined.

Br_2^- , ClBr^-) are involved in THM formation is unknown. If, however, they are involved, then composition factors such as the concentration of inorganic anions may play an important role. High levels of HCO_3^- or CO_3^{2-} would rapidly quench active halogen radicals, thereby limiting CHBr_3 production.

Another interesting facet of Br^- involvement in ClO_2 photolysis is shown in Figures 5 and 6. In these experiments, $1.5 \times 10^{-4} \text{M}$ ClO_2 solutions containing $1 \times 10^{-4} \text{M}$ Br^- were exposed to alternating 12-h light and dark periods. Irradiation during the light periods was supplied by overhead fluorescent room lights. It is apparent from Figure 5 that without added Br^- , no significant ClO_2 decay occurred during the dark periods. When Br^- was present, however, the initial light exposure period apparently generated photoproducts that enhanced the ClO_2 decay reaction during subsequent dark and light exposure periods.

In summary, the nature of the compositional variations that affect ClO_2 decomposition and CHBr_3 formation are still obscure, and the reaction mechanisms are complex.

PHOTOCHEMICAL DECOMPOSITION MODELING

001655

The photolysis rate and half-life of ClO_2 were calculated for waters with organic contents of 0.58, 6.20, and 17.6 mg/L TOC using a modified version of the photochemical model of Zepp and Cline.¹⁷ The photolysis rate is calculated based on the assumption that the loss occurs as a result of primary processes. Any secondary reactions that may lead to a loss of ClO_2 would lead to a faster rate. This model calculates the attenuation of light in the water column resulting from absorption and Rayleigh scattering within the water column itself and from the layer average amount of light absorbed between the surface and a depth D . Solar fluxes at ground level are specified as a function of time of day, season, total ozone column amounts, and the latitude based on the regression analysis of Benner.¹⁸ Other critical input parameters are water absorbance, molar extinction coefficient, and quantum yield, all as a function of wavelength. Except for surface photolysis rates, all other calculated rates represent averages over the depth of shallow holding ponds with weak thermal stratification and sufficiently strong wind. Thermally or mechanically driven mixing cycles the water from the bottom to the surface on a time scale faster

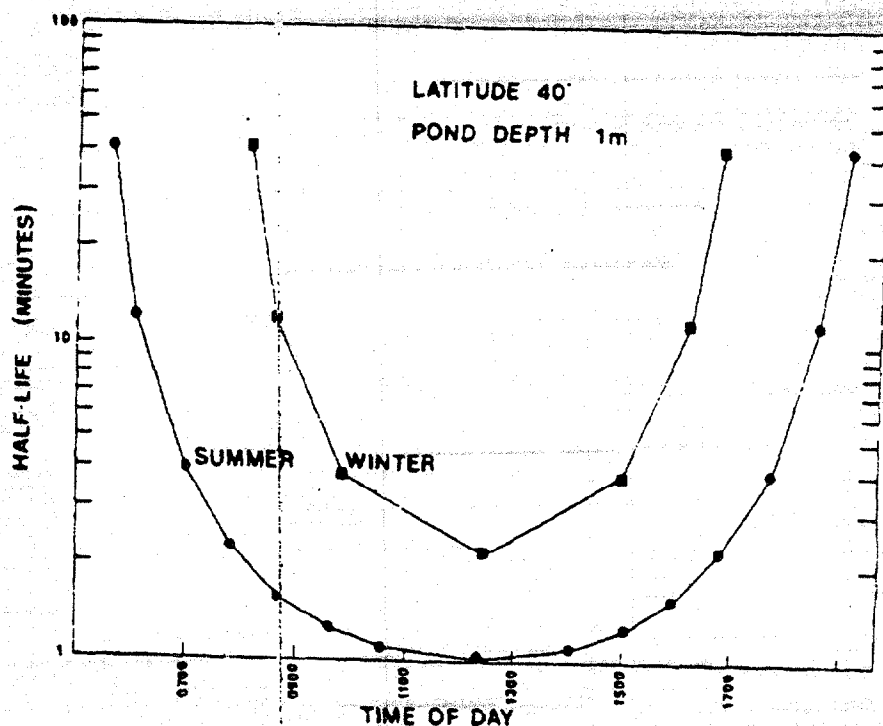


Figure 7. Time-of-day variation in half-life of ClO_2 for sunlight exposure for midsummer and midwinter in contact pond water with a depth of 1 m.

001656

than the half-life because of photolysis, so that photolysis rather than mixing is the rate-limiting step in the destruction of ClO_2 . As the photolysis rate increases, the assumption is no longer valid; the calculated half-life is then only a lower limit, with mixing in the pond becoming the rate-limiting step in the loss process.

The time-of-day variation in the half-life for a 1-m-deep pond at 40° latitude in winter and summer is shown in Figure 7. At midday in summer, the lifetime is about 1 min and is always < 10 min during the daylight hours. In winter, photolysis is only important during the middle 6 h of the day. Figure 8 shows the variation of the half-life with the depth of the holding pond for waters of different clarities ranging from clear to dark-colored (i.e., 17.6 mg/L). For clear water (i.e., 0.53 mg/L), the half-life is nowhere as sensitive to the depth of the pond as for colored water. In 17.6 mg/L, most of the light is absorbed in the upper 10 cm; therefore, the loss rate will be dependent on the strength of the mixing.





Memo

To: Chadd Hermann
From: Yan Wang
CC: Maurice Gutierrez, Gary Kielman, Cayce Warf
Date: April 15, 1998
Re: Chlorite Residual Investigation for LA Water & Power Reservoir Treatment

Introduction

Los Angeles Reservoir has been treated with chlorine to control algae growth. Every year over the last five years 1350 to 1829 tons of chlorine have been used to treat 3.3 billion gallons of water in the reservoir. The chlorination of the reservoir water has resulted in the formation of THMs. The Department of Water and Power has implemented REOS (remote electro-optical sensor) technology to achieve an earlier bloom intervention and to adjust the dosage of chlorine. This adjustment of its treatment strategy has reduced the THM level in the reservoir, however, to comply with the new DBP (disinfection byproduct) regulations (THMs < 0.1 ppm) and to ensure the algae control in the reservoir, alternative technologies are necessary. 0.03

The Department's DBP task team has proposed to investigate the potential benefits of using chlorine dioxide as an algacide to control algae growth, especially to control *Hypnomonas*, which is resistant to chlorine. The byproduct of chlorine dioxide are chloride, chlorite, and chlorate. The proposed Stage 1 DBP Rule includes a maximum contaminant level for chlorite of 1.0 ppm (mg/L). The chlorine dioxide demand of the reservoir water was determined to be around 0.35 mg/L to 0.45 mg/L from previous studies conducted on site. This bench study was carried out to determine the chlorite residual level using 1.0 mg/L of chlorine dioxide to treat the reservoir water.

Conclusion

001657

The decomposition of chlorine dioxide and chlorite increased significantly when exposed to sunlight. When stored in the dark over 6 hours, only 24% of the dosed chlorine dioxide was converted to chlorite (see Figure 1 and Table 2 for sample E). Over 60% of the dosed chlorine dioxide remained in the water after 6 hours in the dark. For the same period of time, when the sample was stored under fluorescent light, 40% of the dosed chlorine dioxide became chlorite (see Figure 1 and Table 2 for sample D). When the treated sample was stored outside the building under daylight, the added chlorine dioxide decayed completely within 2 hours and the chlorite residual was less than 6% of the dosed chlorine dioxide after a 6 hour exposure (see Figure 2 and Table 2 for sample L1).





February 19, 1999

Vera Melnyk-Vecchio, P.E.
 District Engineer, Metropolitan District
 California Department of Health Services
 Office of Drinking Water
 1449 West Temple Street, Suite 202
 Los Angeles, California 90026-5698

Dear Ms. Melnyk-Vecchio:

Preliminary Evaluation of Chlorine Dioxide at Los Angeles Reservoir

Enclosed is the evaluation report for our chlorine dioxide study at Los Angeles Reservoir. The test was conducted between October 8-10, 1998 and was a success in many ways.

Algae was successfully arrested during the application with no trihalomethanes formed. The reservoir was put back in service with all the levels of by-products being met under the guidelines set forth.

We are planning to test chlorine dioxide again as an algaecide in a flow-through environment at the reservoir sometime this year. We will notify you before this test begins. Thank you for your guidance and assistance throughout this study.

If you have any questions concerning this matter, please contact me at (213) 367-3193 or Mr. Paul E. Liu at (213) 367-0761.

Post-it® Fax Note	7671	Date	2/31	# of pages	B
To	CAYU WAF	From	GARY STOLARIK		
Co./Dept.		Co.			
Phone #		Phone #	213-367-3193		
Fax #	425-661-0143	Fax #			

Sincerely,
 Original Signed By
 GARY F. STOLARIK

GARY F. STOLARIK
 Engineering Manager

FCL:am

Enclosure

c: Mr. Paul E. Liu

bc: Larry McReynolds Robert Y. Yoshimura John D. Miller Mark B. Osokow
 Cecilia K.T. Weldon Richard F. Harasick William M. Heyer Daniel L. Saenz
 Gerald A. Gewe Scott J. Munson Douglas B. Ball J. Donald Christie 001658
 Pankaj Parekh Ali A. Karimi Gary D. Bishop Morley W. Male
 David W. Heumann James B. McDaniel Marina J. Busatto Gary M. Pintar
 Jose L. Ancheta James G. Yannotta Jay Negrin Brian N. White

File: DBP- Chlorine Dioxide

To: California Department of Health Services
From: Los Angeles Department of Water and Power
Subject: Preliminary Evaluation of Chlorine Dioxide at Los Angeles Reservoir

SUMMARY

The Los Angeles Department of Water and Power (LADWP) tested chlorine dioxide (ClO_2) as an algaecide at the Los Angeles Reservoir (LAR) from October 8, 1998 to October 10, 1998. LAR was isolated from service during the study. A total of about 28,000 pounds of ClO_2 were generated for nine hours on the first night (10/8-9/98) and six hours on the second night (10/9-10/98). ClO_2 was applied after sundown to avoid rapid photodecomposition when exposed to sunlight. The three main findings are:

- Rising chlorophyll levels due to *Hypnomonas* were arrested and reduced by 47%;
- LAR stayed within the Department of Health Services (DHS) limits for chlorine dioxide, chlorite, and chlorate;¹⁾
- Total trihalomethanes (TTHMs) were not formed with the levels decreasing slightly by the end of the study.

LADWP proposes to test ClO_2 in a flow-through environment next spring 1999 before making a recommendation on implementation of this algaecidal technology at LAR.

BACKGROUND

A proposal to study ClO_2 at LAR was submitted to DHS dated April 20, 1998. The proposal detailed the current strategy for monitoring and controlling algae at LAR using chlorine, the proposed ClO_2 equipment setup, the experimental constraints, and the special monitoring and sampling during the experiment. There were three main objectives listed in the proposal. ClO_2 would be evaluated by its ability to:

- Rapidly control algae and especially *Hypnomonas* in nocturnal applications;
- Minimize total TTHMs and Haloacetic acids (HAAs) while limiting its own byproducts of chlorite and chlorate;
- Back up chlorine as an algaecide for use as a strategic, cost-effective treatment.

EQUIPMENT OPERATION AND SAMPLING PLAN

Three 12,000 lb/day ClO_2 generators and two 7,000-gallon sodium chlorite tanks were installed for temporary use at LAR. ClO_2 generation efficiencies over 95% were measured and maintained throughout the experiment. ClO_2 solution was discharged through three headers within LAR (see Figure 1). Four Flygt propeller mixers aided distribution throughout the reservoir. Water samples were collected at two locations: near the outlet tower (TWR) and near the center of the reservoir (CTR). Samples were collected 3m below the surface and 1.5m above the bottom at both locations. The Sampling, Monitoring, and Contingency Plan (Appendix A) presents additional information and sampling schedules.

001659

ClO2/QFS/PEL/2/19/99

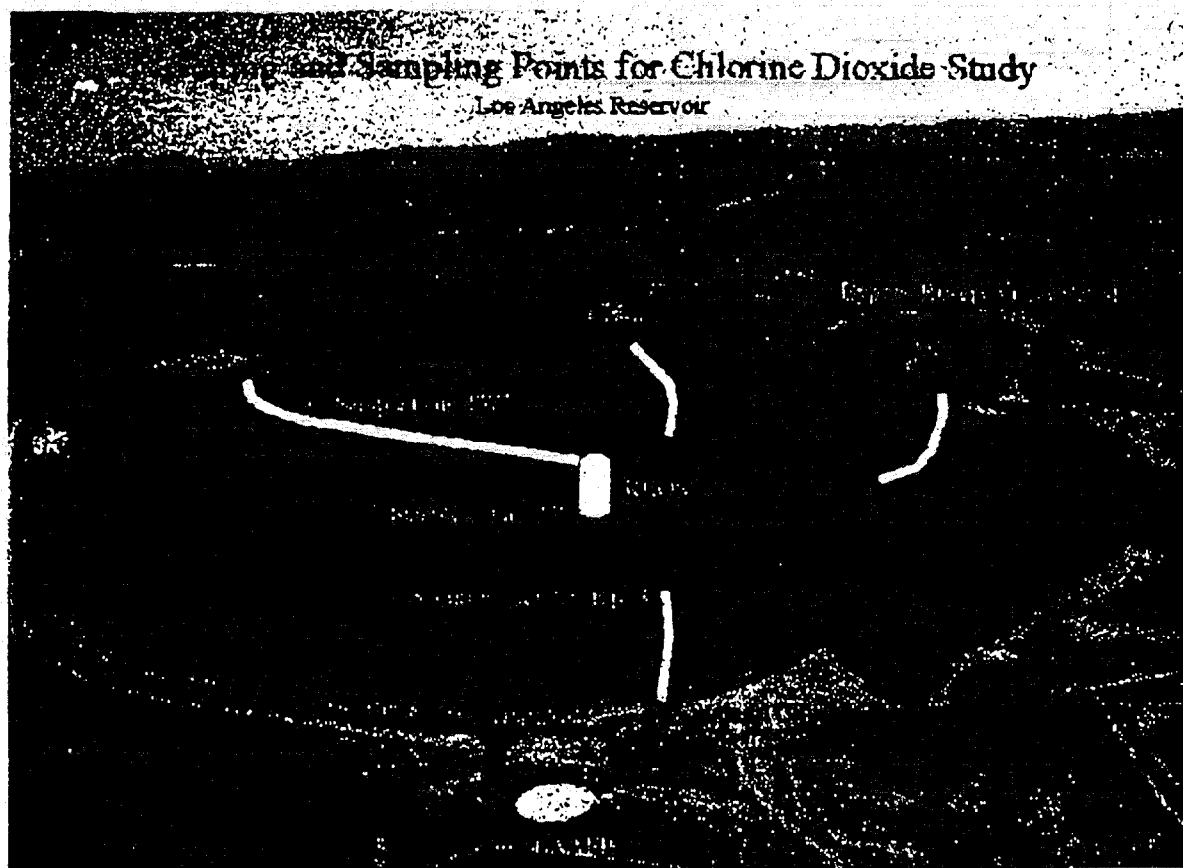


Figure 1 - not to scale; view is southerly from LAAFP

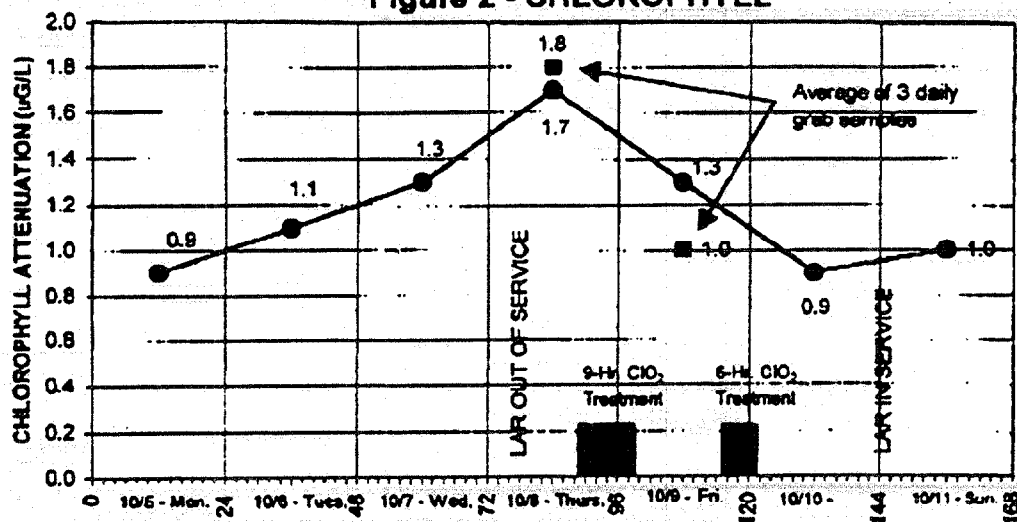
ALGAE MONITORING AND CONTROL

Planktonic algal growth in LAR is continuously monitored during daylight hours with a moored Remote Electro Optical Sensor (REOS) system located near the CTR sampling station. Site-specific relationships between weekly field-chlorophyll data and daily REOS optical data support the daily REOS chlorophyll estimates used to guide chlorination operations according to simple biomass and rate of change criteria. REOS provides two chlorophyll estimates based on independent light attenuation and algal fluorescence measurements. REOS has proven to be a powerful tool in the early detection and economical control of algal blooms at LAR^[2].

LAR was isolated from outflow around 1:30 PM on Thursday, October 8 after determining nuisance levels of *Ilypnomonas*. Pre-filter chlorination was also turned off that morning at the Los Angeles Aqueduct Filtration Plant (LAAFP). Figure 2 is a graph of the chlorophyll values (based on attenuation) starting from Monday, October 5 through Saturday, October 10. The chlorophyll started at a value of 0.9 µg/L on October 5 and rose to 1.7 µg/L on October 8 before treatment commenced. ClO₂ generation started at 6:30 PM on October 8 and ended at 3:30 AM the next morning. An approximate dose of 0.9 mg/L of ClO₂ was achieved based on the volume of LAR which was 2.2 billion gallons at the time. Following this application, the chlorophyll value dropped to 1.3 µg/L the next day (10/9). Treatment started again at 7:15 PM that night and ended at 1:15 AM the next day (10/10) for an applied dose of 0.6 mg/L. The final chlorophyll reading was 0.9 µg/L by sundown on October 10. This represents a 47% reduction in chlorophyll over the course of treatment $[(1.7-0.9)/1.7 = 47\%]$.

001660

Figure 2 - CHLOROPHYLL

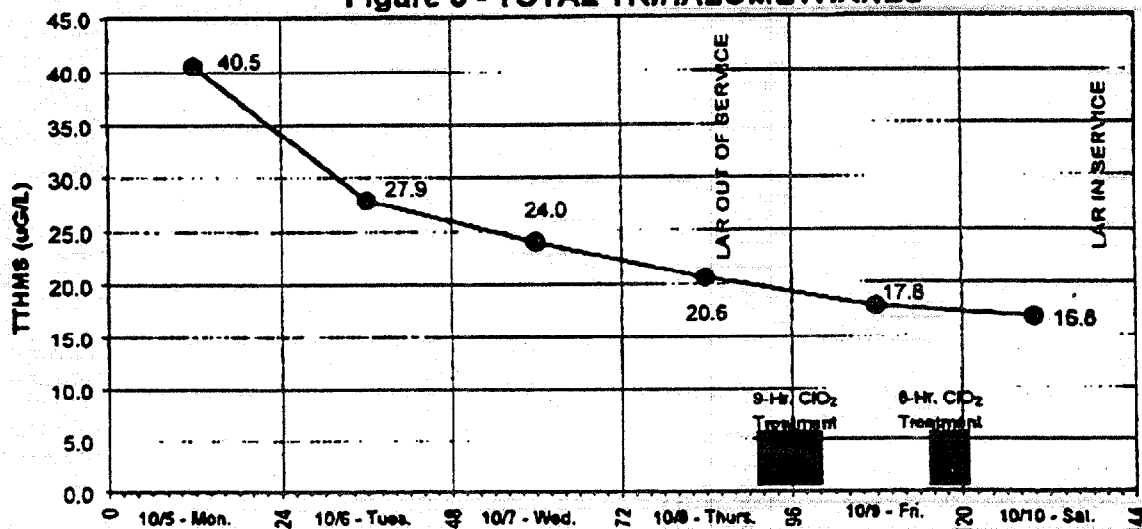


ANALYTICAL RESULTS

TTHM Formation

The four constituents that make up TTHMs are bromodichloromethane, bromoform, chloroform, and dibromochloromethane. The Stage 1 DBP MCL for TTHMs has been lowered to 80 µg/L with the standard expected to go as low as 40 µg/L by Stage 2 implementation in 2002. The chloroform MCL goal is 0 µg/L. During the experiment, LAR TTHMs started at 20.6 µg/L on October 8 and ended at 16.8 µg/L on October 10. The results indicate that ClO₂ did not react with precursors to form TTHMs in this application. The declining TTHM levels are most likely due to volatilization, degradation, and from earlier cessation of pre-filter chlorination before ClO₂ was turned on. TTHMs are shown in Figure 3.

Figure 3 - TOTAL TRIHALOMETHANES



001661

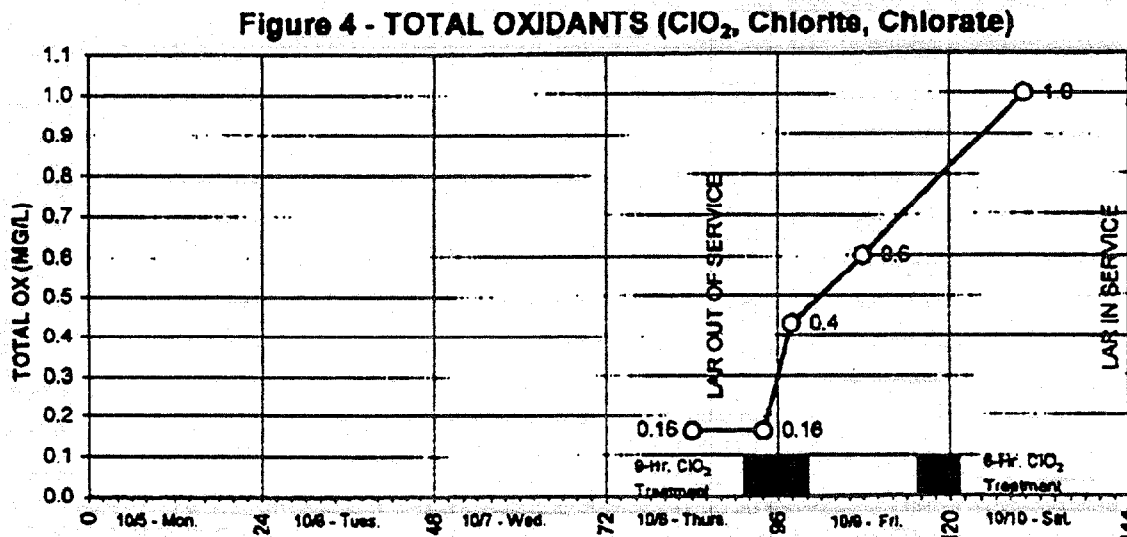
Unfortunately, HAAs were not monitored during the experiment because of personnel and time constraints. HAA sampling will be included in future ClO_2 tests. Microcosm studies will also be performed which will compare chlorine and ClO_2 side by side in a controlled environment.

Chlorine Dioxide, Chlorite, and Chlorate Formation

Chlorite and chlorate are the main by-products of ClO_2 . Previous studies conducted at LA AFP^[3] supported the literature that ClO_2 and chlorite would photodecompose to chlorate^[4]. The criteria set forth by DHS for this study before LAR was to be put back into service were^[1]:

- ClO_2 not to exceed 0.8 mg/L;
- Chlorite not to exceed 1.0 mg/L;
- Total oxidants (ClO_2 , chlorite, and chlorate) not to exceed 1.0 mg/L;

LADWP established control of the algal bloom and met all three criteria on the evening of Saturday October 10. A call was placed to Ms. Vera Melnyk-Vecchio of DHS who gave regulatory approval of acceptable byproduct levels^[5]. The reservoir was placed in service at approximately 12:30 AM, October 11. Figure 4 shows the average sum of the total oxidants (ClO_2 , chlorite, and chlorate) for all samples collected throughout the study. Table 1 presents the tabulated results. There was an initial chlorate value of 0.16 mg/L when the study began on October 8. The first sampling run between 10:00-11:00 PM, (10/8), showed no ClO_2 residual; however, the second sampling run between 1:00-2:00 AM (10/9) did show a ClO_2 residual, chlorite and additional chlorate levels. Additional samples were collected between 1:00-2:00 PM under clear skies on both October 9 and 10. As expected, ClO_2 had completely volatilized with only small traces of chlorite (< 0.1 mg/L) left in the afternoon samples.



001662

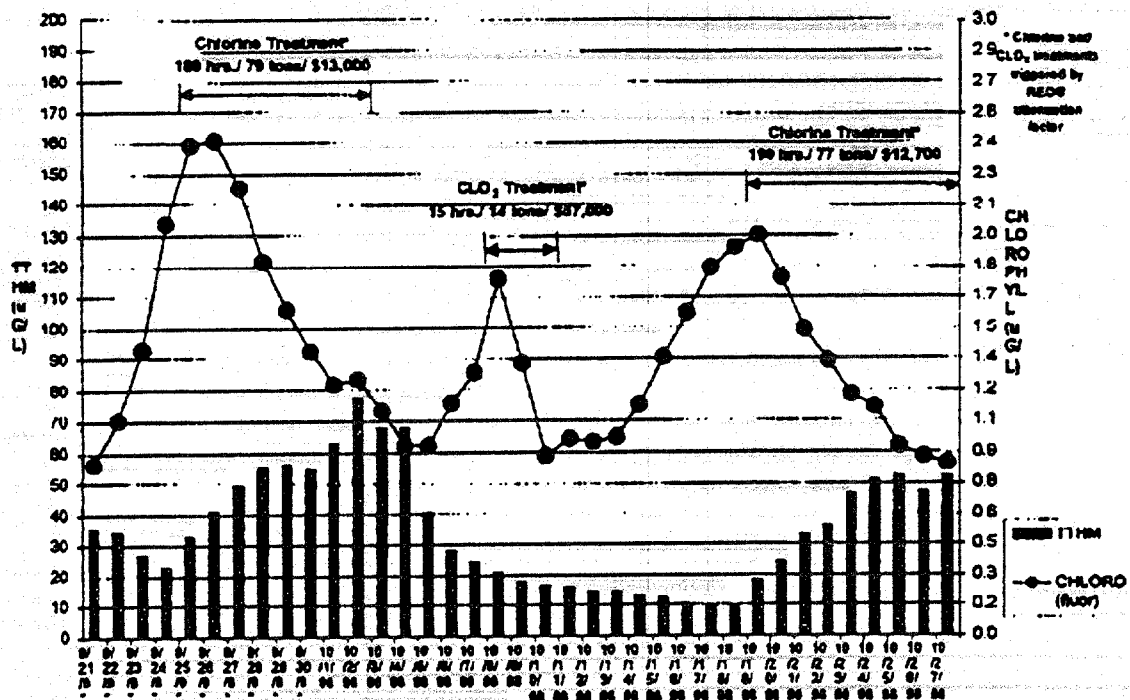
TABLE 1					
BASELINE DATA (OCT. 8TH)		ClO ₂	CHLORITE	CHLORATE	TOTAL
		mg/L	mg/L	mg/L	mg/L
		0.00	0.00	0.16	0.16
SAMPLE RUN TIME (OCTOBER 9TH, 1AM-2AM)					
LOCATION	DEPTH	ClO ₂	CHLORITE	CHLORATE	TOTAL
	meters	mg/L	mg/L	mg/L	mg/L
Tower	3.0 from surface	0.37	0.10	0.21	0.68
Tower	1.5 from bottom	0.00	0.11	0.19	0.30
Center	3.0 from surface	0.00	0.05	0.17	0.22
Center	1.5 from bottom	0.21	0.09	0.19	0.49
AVERAGE		0.1	0.1	0.2	0.4
SAMPLE RUN TIME (OCTOBER 9TH, 1PM-2PM)					
LOCATION	DEPTH	ClO ₂	CHLORITE	CHLORATE	TOTAL
	meters	mg/L	mg/L	mg/L	mg/L
Tower	3.0 from surface	0.00	0.03	0.65	0.68
Tower	1.5 from bottom	0.00	0.11	0.66	0.77
Center	3.0 from surface	0.00	0.05	0.45	0.50
Center	1.5 from bottom	0.00	0.08	0.39	0.47
AVERAGE		0.0	0.1	0.5	0.6
SAMPLE RUN TIME (OCTOBER 10TH, 1PM-2PM)					
LOCATION	DEPTH	ClO ₂	CHLORITE	CHLORATE	TOTAL
	meters	mg/L	mg/L	mg/L	mg/L
Tower	3.0 from surface	0.00	0.06	1.07	1.13
Tower	1.5 from bottom	0.00	0.07	1.07	1.14
Center	3.0 from surface	0.00	0.06	0.76	0.82
Center	1.5 from bottom	0.00	0.11	0.91	1.02
AVERAGE		0.0	0.1	1.0	1.0

COMPARISON WITH CHLORINE

Figure 5 is a comparison of the average daily chlorophyll values (dots) from REOS and the TTHM values (bars) of the two chlorine treatments that happened before and after the ClO₂ study. The first chlorine treatment lasted for 189 hours over 8 days (9/25-10/2) and used 79 tons of chlorine. The second chlorine treatment lasted for 190 hours over 9 days (10/19-10/27) and used 77 tons of chlorine. The ClO₂ treatment in between used 14 tons of ClO₂ and lasted 15 hours. The rate of decline of chlorophyll during the ClO₂ study was -0.4 µg/L/day, which was twice the rate for the before-and-after chlorine treatments (-0.2 µg/L/day). The estimated cost of \$57,000 for the ClO₂ study was at least four times as expensive as chlorine to handle an algae episode during this period. TTHMs were at their lowest values after the ClO₂ treatment and before the start of chlorine treatment.

001663

Figure 5 - CHLORINE DIOXIDE VS. CHLORINE



FLOW-THROUGH SCENARIO

LADWP hopes to test ClO₂ in a reservoir flow-through experiment in order to complete its evaluation of the algaecide. The flow-through will alter the reservoir's circulation and may affect the distribution of ClO₂ within LAR.

With the promulgation of the Stage 1 DBP Rule on December 6, 1998, LADWP will henceforth comply with all limits and monitoring requirements that are set in the Federal Register. The regulations concerning ClO₂, chlorite, and chlorate are:

ClO₂:

0.8 mg/L

Daily sampling at the entrance to the distribution system

Chlorite:

1.0 mg/L

Daily sampling at the entrance to the distribution system

Monthly sampling at nearest, mid- and furthest consumer sample

Chlorate:

Not regulated

001664

The current regulations do not specify requirements for chlorate; however, LADWP will sample and monitor for chlorate daily at the entrance to the distribution system and monthly at the nearest, mid- and furthest consumer sample locations. TTHMs and HAAs will also be monitored daily at the entrance to the distribution system while other constituents listed in the original sampling plan [Appendix A] will be monitored before and after the application. LADWP will

notify sensitive populations if the levels of ClO_2 and chlorite are anticipated to be above the limits set forth.

LADWP will use the Lissamine Green B Spectrophotometric Method^[6] for ClO_2 residual analysis. This method is quicker and more accurate than the Amperometric 4500E Method and has been recommended by experts in the field^[7,8]. Chlorite and chlorate analysis will be performed by the IC 300 Method.

LADWP will notify DHS when this scenario is about to commence and will forward results and evaluations.

CONCLUSION

ClO_2 was an effective algacide with a chlorophyll decline rate twice that of chlorine in sequential algal episodes treated at LAR. The amount of ClO_2 generated was less than 5.5 times that of the chlorine treatments. TTHMs were not formed during the study. Approximately 67% of the ClO_2 applied reduced to chlorate. A 1.0 mg/L total oxidants criteria was imposed for this study which limited the amount of ClO_2 that could be applied on a given evening. However, the proposed Stage 1 DBP regulations have set limits for ClO_2 and chlorite but not for chlorate.

The next step is to test ClO_2 at LAR while the reservoir is in service in order to provide further understanding of the effectiveness of ClO_2 in controlling algae.

REFERENCES

1. Stolarik, G. and Liu, P. "Letter to Mr. Gary Yammamoto Concerning Limits for ClO_2 Study." Los Angeles Department of Water and Power (August 11, 1998)
2. White, B. and Stolarik, G. "Algal Control Demonstration-Los Angeles Reservoir." Los Angeles Department of Water and Power (June 1998)
3. Zika, R., et al. "Sunlight-Induced Photodecomposition of Chlorine Dioxide." Water Chlorination Environmental Impact and Health Effects Vol. 5 (1985)
4. Wang, Y. "Memo: Chlorite Residual Investigation for LA Water and Power Reservoir Treatment." Vulcan Chemical Technologies, Inc. (April 15, 1998)
5. Personal Communication between Ms. Vera McInyk Vecchio (DHS) and Mr. Gary Stolarik (LADWP), October 10, 1998
6. Bubnis, B. "Chlorine Dioxide Measurement Using Lissamine Green B." Novatek, (January 1997)
7. Gates, D. "Practical Suggestions for Meeting USEPA Compliance Monitoring Requirements and in-plant Operational Control of Chlorine Dioxide in Drinking Water" International Ozone Association Pan-American Group Conference Proceedings, Vancouver, Canada (October 18-21, 1998)
8. Personal Communication between Dr. Gilbert Gordon (University of Miami Ohio, Chemistry Department) and Mr. Paul Liu (LADWP), November 16, 1998.

001665



**CHLORINE DIOXIDE:
DRINKING WATER ISSUES**

Conference Proceedings

**May 7-8, 1992
Houston, Texas**

**Sponsored by
AWWA Research Foundation
and
Chemical Manufacturers Association
and
U.S. Environmental Protection Agency**

001666

**Published by
AWWA Research Foundation
American Water Works Association**

EN



MUTAGENIC ACTIVITY IN HUMIC WATER AND ALUM FLOCCULATED HUMIC WATER
TREATED WITH ALTERNATIVE DISINFECTANTS *WLR*

P. Backlund¹, L. Kronberg¹, G. Pensar¹ and L. Tikkanen²

¹Department of Organic Chemistry, Abo Akademi, SF-20500 Turku,
Finland *(84) (94) (82)*

²Technical Research Centre of Finland, Food Research Laboratory,
SF-02150 Espoo, Finland *(82) FI*

ABSTRACT

Mutagenic activity in *Salmonella typhimurium* strains TA 100, TA 98 and TA 97 has been determined for humic water and alum flocculated humic water, treated with the alternative disinfectants chlorine, ozone, chlorine dioxide, ozone/chlorine and chlorine/chlorine dioxide.

The most pronounced activity was found for chlorine treated water tested on strain TA 100 without metabolic activation (S9 mix). Ozone treatment prior to chlorination did not alter the activity, while treatment with chlorine in combination with chlorine dioxide reduced the activity to a level somewhat over the background. No mutagenic response was detected in waters treated with ozone or chlorine dioxide alone. In presence of S9 mix all water extracts studied were non-mutagenic.

INTRODUCTION

Municipal drinking water is generally supplied from surface water in nearby rivers or lakes. In Finland humic substances comprise by far the major portion of the organic material present in surface waters (TOC 10-30 mg/l), while the contribution of anthropogenic compounds usually is small.

During water purification, using conventional treatment practices (flocculation, sedimentation and filtration), 70-80 % of the humic material is removed from the water. The remaining organics are subjected to the oxidizing effect of water disinfectants.

During the last decade there have been several reports on mutagenic activity in concentrates of chlorine treated waters (Cheh et al. 1980, Kool et al. 1982, Marouka et al. 1983). The influence of other disinfectants on the mutagenic activity of water has, however, been studied to a more limited extent. Zoeteman et al. (1982) have reported an increase of direct acting mutagens in sur-

face water after treatment with chlorine dioxide (strains TA 100 and TA 98). In the same study ozone treatment of raw water was found to reduce mutagenic activity in strain TA 98 both with and without metabolic activation. Increased mutagenic activity has been reported in water containing soil fulvic acid after treatment with ozone in combination with chlorine (Kowbel et al. 1984).

In the present study mutagenic activity in *Salmonella typhimurium* strains TA 100, TA 98 and TA 97 was determined for humic water (HW) and alum flocculated humic water (FHW), treated with the alternative disinfectants chlorine, ozone, chlorine dioxide, chlorine/chlorine dioxide and ozone/chlorine. The resulting response patterns of humic water and alum flocculated water were compared in order to test the hypothesis that mutagenic compounds are produced as a result of reactions between disinfectants and humic substances (Meier et al. 1983, Kronberg et al. 1985).

MATERIALS AND METHODS

Non-mutagenic natural humic water (see Table 1) was collected from a lake (Savojärvi) situated in a marsh region in the southwestern part of Finland, and treated according to the scheme shown in Fig. 1.

Alum flocculation was performed in the laboratory by adding an aqueous solution of $Al_2(SO_4)_3 \cdot 18 H_2O$ to humic water (pH 5.9) while stirring. After settling the clear water was decanted for further treatment.

TABLE 1

Total organic carbon contents of water samples studied and disinfectant dosages applied.

	TOC - value (mg/l)	Cl ₂ - dosage (mg/l)	O ₃ - dosage (mg/l)	ClO ₂ - dosage (mg/l)	Cl ₂ /ClO ₂ - dosage ² - (mg/l)	O ₃ /Cl ₂ - dosage (mg/l)
Humic water	21.0	21.0	10.0	21.0	10.5/10.5	10.0/21.0
Alum flocc. humic water	6.4	6.5	2.9	6.5	3.25/3.25	2.9/6.5

001668

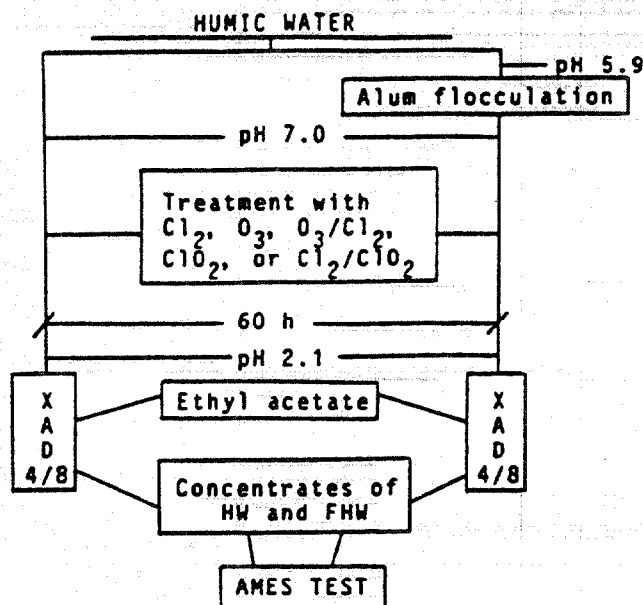


Fig. 1. Scheme of water treatment.

Prior to disinfection pH of the water samples was adjusted to 7.0 by adding 4 M NaOH and a potassium phosphate buffer.

Chlorine- and chlorine dioxide treatments were carried out at room temperature using freshly made stock solutions in distilled water.

The chlorine solution was prepared by bubbling chlorine gas (generated by adding fuming HCl to KMnO₄, with subsequent cleaning and drying) into a solution of 2.3 % NaOH until a pH of 7-8 was obtained. The concentration of chlorine in the solution was determined by the starch-potassium iodide technique.

The chlorine dioxide stock solution was prepared by adding a solution of HCl (9 %) to aqueous 7.5 % NaClO₂. The resulting chlorine dioxide gas was swept off from the mixing bottle by nitrogen and collected in buffered (pH 7.0) distilled water. The concentration of chlorine dioxide in the solution was determined by the starch-potassium iodide method.

Ozonation was performed using a laboratory ozonator (Herrman-Labor Lo-50-1) with a maximum capacity of 7 g O₃/h. Oxygen was used as feed gas. The ozone concentration in the gas stream was determined both before and after ozonation by the starch-potassium iodide technique.

001669

The ratio of TOC to the amount of chlorine or chlorine dioxide added to the water was 1:1, resulting in a residual concentration of 0-0.2 mg/l after a reaction time of 60 h at room temperature in the dark. Noack et al. (1978) have shown that treatment of water containing humic acid with a chlorine/chlorine dioxide mixture of 1:1 (w/w) minimizes the combined formation of chloroform and chlorite. For this reason the chlorine/chlorine dioxide treatment was carried out by adding a mixture of 1:1 of the two disinfectants at a ratio of TOC to total disinfectant of 1:1. The ozone dosage applied to humic water and alum flocculated humic water was 10 mg/l and 2.9 mg/l respectively. In the combined ozone/chlorine treatment, ozonation was performed 2 h prior to chlorination. We have noticed in earlier experiments that pre-ozonation of water containing humic substances does not significantly influence the chlorine consumption of the water. For this reason the chlorine dosage applied after ozonation was equal to that applied when using chlorine alone, and, consequently, resulting in a residual chlorine concentration of 0-0.2 mg/l after 60 h reaction time.

Prior to concentration on XAD 4/8, pH of the water was adjusted to 2.1 (4 M HCl). The adsorbed organics were eluted by ethyl acetate and, prior to assay, the solvent was replaced by DMSO. The concentration procedure used has previously been described in detail (Kronberg et al. 1985). The largest equivalent volumes of water extracts tested were 50 ml and 200 ml for humic water and flocculated humic water respectively.

Mutation tests were performed according to the method of Ames (Ames et al. 1975) with minor modifications (von Wright et al. 1978). The *Salmonella typhimurium* tester strains TA 100, TA 98 and TA 97 were provided by Dr. B.N. Ames, University of California. When metabolic activation was used, liver homogenate (S9mix) was prepared from the livers of male Sprague-Dawley rats induced with Na-phenobarbital and β -naphthoflavone (Matsushima et al. 1979).

The test results are means of duplicate plates and each test was repeated at least once.

RESULTS

Mutagenic activity was found in chlorinated water concentrates when tested on strains TA 100, TA 98 and TA 97 without enzyme activation (see Fig. 2). The highest responses were noted for strain TA 100.

001670

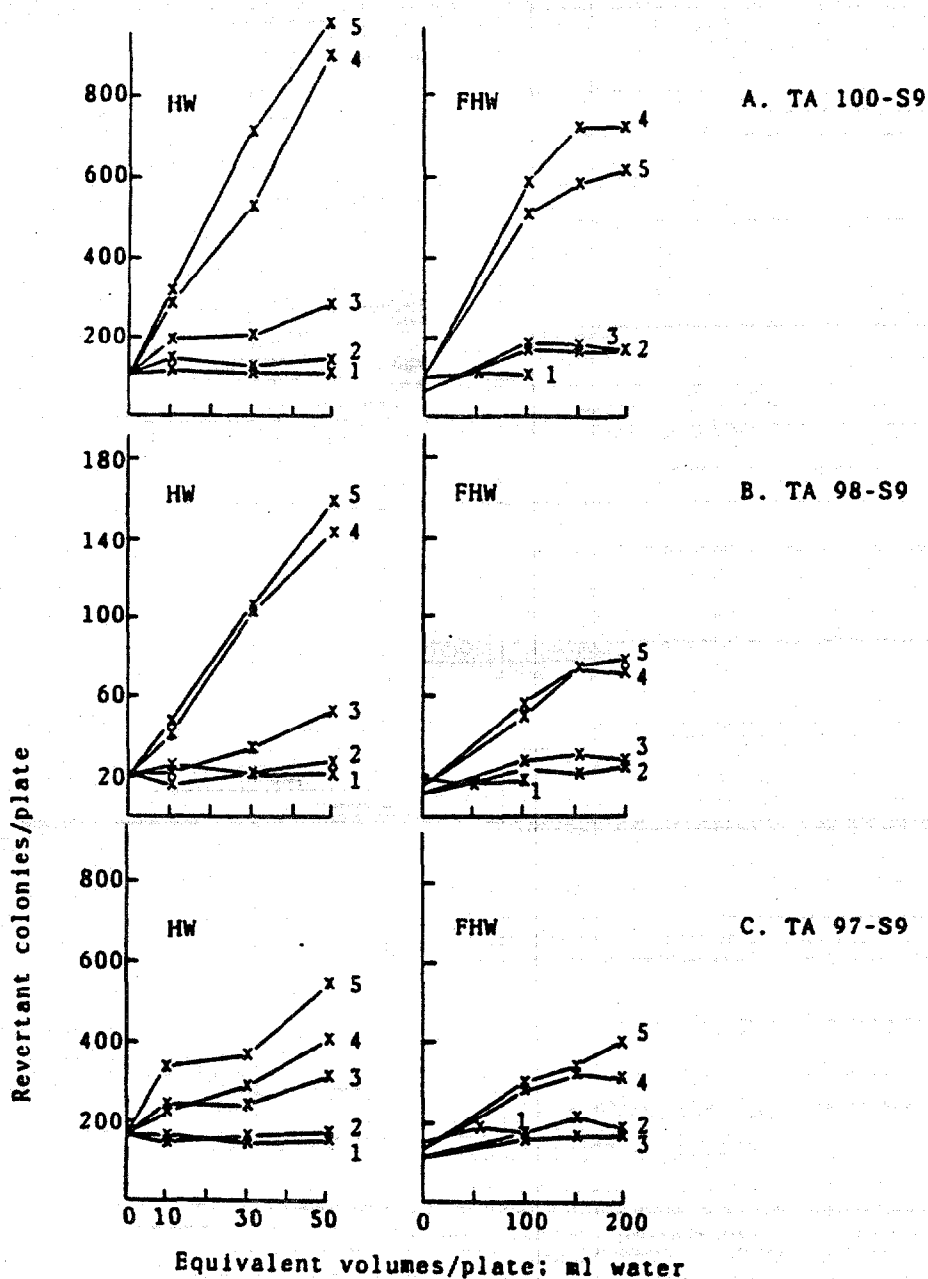


Fig. 2. Mutagenic response of strains TA 100 (A), TA 98 (B) and TA 97 (C) (-S9mix) for humic water and alum flocculated humic water treated with 1. ozone, 2. chlorine dioxide, 3. chlorine/chlorine dioxide, 4. chlorine, 5. ozone/chlorine.

001671

TXL 01671

Research Letters

**IODINATION OF NUTRIENTS IN THE PRESENCE OF CHLORINE
BASED DISINFECTANTS USED IN DRINKING WATER TREATMENT**

(Iodinated nutrients; dietary iodide; monochloramine; chlorine dioxide; chlorine;
drinking water disinfectants)

J.P. BERCZ and R. BAWA

Toxicology and Microbiology Division, Health Effects Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH 45268 (U.S.A.)

(Received 8 October 1985)

(Accepted 26 August 1986)

SUMMARY

Under conditions simulating the gastrointestinal tract chlorine dioxide (ClO_2), HOCl , and NH_2Cl caused covalent organification of iodide to nutrient biochemicals. The extent of binding seemed to be proportional to the electromotive force (EMF) and stoichiometry of the redox couple between iodide and the oxidant. Almost half of 71 nutrients examined were found to bind reactive iodine. Iodide was found to inhibit the quinoidal chromogen formation from tyrosine and ClO_2 , demonstrating the preferential generation of reactive iodine in complex organic mixtures. These findings indicate that ingestion of residual disinfectants via drinking water may pose a health risk in terms of in vivo generation of iodinated organics. Structure, formation, and biological activity of these compounds are under study.

INTRODUCTION

Ongoing in vivo toxicology studies with ClO_2 in this laboratory provided evidence that disinfectants cause covalent immobilization of iodide in the gastrointestinal tract of rats [1]. ClO_2 administered via drinking water was also demonstrated to inhibit thyroxine synthesis in monkeys [2], raising suspicion that this effect may be caused by some thyroid inhibitory substance formed in the alimentary tract. This possibility necessitated the study of the redox interaction between iodide and nutritional biochemicals and complex nutrients in the presence of disinfectants.

001672

MATERIALS AND METHODS

Nutritional biochemicals and some complex nutrients were purchased from the Sigma Chemical Company (St. Louis, MO), and other complex nutrients were taken from biological samples. Carrier-free ^{125}I as NaI was purchased from the New England Nuclear Company (Boston, MA). Saliva and gastric juice were obtained from Rhesus monkeys under mild anesthesia by intubation. Gastric juice flow was induced by a single i.v. injection of pentagastrin at 5 $\mu\text{g}/\text{kg}$ dose. Preparation and assay of disinfectants in double-distilled deionized water was referenced elsewhere [2]. Prefilled 0.8 cm \times 4 cm AGI-X8(Cl^-) anion exchange columns were purchased from the Bio-Rad Company (Richmond, CA). This resin quantitatively traps inorganic iodide and allows total recovery of covalently bound iodine by elution with 8 N acetic acid.

Iodination procedure

Tyrosine was used as a reference test compound to establish optimal reactant ratios. Depending on their solubilities, the substrates were dissolved in solvents as listed in Table 1. To 1 ml of 0.02 N HCl was added 0.1 ml of 0.1 M KI, containing 9×10^5 cpm $^{125}\text{I}^-$, and 0.3 ml of 600 ppm disinfectant in a capped conical polystyrene centrifuge tube. To this mixture was added either 2 ml of 0.01 M simple nutrient molecule solution, 2 ml of 10 mg/ml complex nutrient solution, or 100 μl of saliva or gastric juice. After mixing, the reaction was allowed to proceed at room temperature for 10 min and was stopped by the addition of 0.2 ml of 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$. Distilled water instead of HCl was used in NH_2Cl reactions. The final reaction mixture was transferred to an anion exchange column and eluted with 4–8 \times 1 ml aliquots of 8 N CH_3COOH . The amount of eluent required varied with each individual substance tested. Specific activity of each eluate was determined by counting using the Packard Tricarb Auto-Gamma Scintillation Spectrometer at 93% efficiency. Extent of organification was calculated as percentage of iodide eluted from the columns.

Spectral determination of quinoidal chromogen

Solutions of 2.2 mM ClO_2 , 1.0 mM tyrosine and 0.1 M KI were prepared in distilled water. The first two solutions were mixed in a 1:1 ratio in an erlenmeyer flask (total volume of 3 ml). The color was allowed to develop for 15 min. The resultant solution was diluted 1:1 with distilled water. A UV/visible scan was obtained using 1 cm quartz cuvettes in a Perkin-Elmer 552 double-beam spectrophotometer. The procedure was repeated by adding 0.1 ml of the KI solution first to the tyrosine, followed by the addition of the ClO_2 solution. A dilution of 3:1 with distilled water was made, and a scan was obtained.

TABLE I

EFFECT OF DRINKING WATER DISINFECTANTS ON THE IN VITRO ORGANIFICATION OF IODIDE WITH NUTRITIONAL ORGANICS

Nutrient Substance	% I ⁻ bound in the presence of			Solvent for su
	ClO ₂	Cl ₂	NH ₃ Cl ⁺	
Simple nutrients				
Tyrosine	51.10	22.42	7.60	pH9-NaOH
4-Aminobenzoic acid (PABA)	12.84	0.23	1.06	H ₂ O
B-Sitosterol	11.72	0.08	0.06	CH ₃ OH-ether
Prostaglandin F1 α	10.86	-	-	CH ₃ OH
Arachidonic acid	9.26	2.93	1.48	pH9-NaOH
Folic acid	5.09	0.84	1.72	pH9-NaOH
Pyridoxal	4.24	0.07	0.05	H ₂ O
Thioctic acid	2.73	0.01	1.47	pH9-NaOH
Cholesterol, water-soluble	2.13	0.17	0.19	H ₂ O
Cholecalciferol	2.12	0.97	0.58	CH ₃ OH
Retinoic acid	1.57	1.21	0.38	pH9-NaOH
Biotin	0.80	0.06	0.18	pH9-NaOH
Pyridoxamine	0.71	0.07	0.05	H ₂ O
Vitamin K ₁	0.69	0.08	0.14	C ₂ H ₅ OH
Histidine	0.42	0.08	0.28	H ₂ O
Pyridoxine	0.29	0.07	0.07	H ₂ O
Uridine	0.23	0.07	0.06	H ₂ O
Cytidine	0.21	0.07	0.04	H ₂ O
Cholic acid, Na salt	0.14	0.10	0.03	H ₂ O
Tryptophan	0.13	0.08	0.35	H ₂ O
Glutamic acid	0.10	0.08	0.26	H ₂ O
Complex nutrients				
Gastric juice (monkey)	30.68 ^b	-	-	None
	2.26 ^c	0.28	0.53	H ₂ O
Saliva (monkey)	30.20 ^b	-	-	None
	2.10 ^c	0.07	5.30	H ₂ O
Polyoxyethylene (20)-sorbitan oleate (Tween-80)	26.40	1.12	0.29	H ₂ O
Globulin (bovine)	12.56	0.20	8.86	H ₂ O
Hemoglobin (human)	4.36	0.48	4.11	H ₂ O
Meat extract (peptone)	3.46	1.23	5.60	H ₂ O
RNA (calf thymus)	3.20	0.09	1.64	pH9-NaOH
Corn oil (mazola)	3.00	0.42	0.12	1% Tween
DNA (calf thymus)	2.40	1.37	1.30	pH9-NaOH
B-Lactoglobulin (bovine milk)	0.48	0.00	0.57	H ₂ O

*Hydrochloric acid was not used in the mixture.

^b1.0 ml of undiluted secretion was used.

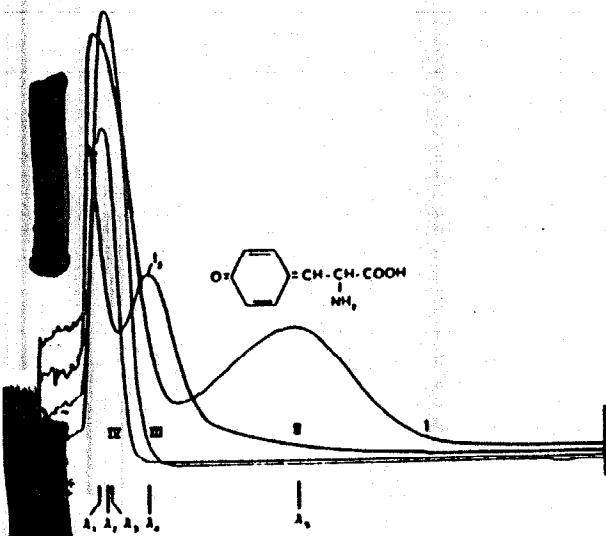
^cPerformed on 0.1 ml fluid diluted to 2 mls.

001673

TABLE II

NUTRIENTS WHICH ORGANIFY IODIDE WITH LESS THAN 0.1% EFFICIENCY IN THE PRESENCE OF ClO_2

Amino acids	Vitamins and cofactors	Nucleotide bases	Sugars and organic acids
Phe. Alanine	Menadione	Adenosine	α -Lactose
Alanine	Riboflavin	Guanosine	Maltose
Arginine	Thiamine	2',3'-Guanosine-5'- PO_4	D-Ribose
Asparagine	Pantothenic acid	2',3'-Uridine-5'- PO_4	D(+)Mannose
Cysteine	Nicotinamide	2',3'-Adenosine-5'- PO_4	D(+)Malic acid
Glycine	NADP	2',3'-Cytidine-5'- PO_4	Corn Starch
Isoleucine	Tocopherol	2'-Deoxyadenosine	
Leucine		2'-Deoxyguanosine-5'-(PO_4) ₃	
Lysine		2'-Deoxyadenosine-5'-(PO_4) ₃	
Methionine			
Proline			
Serine			
Valine			
Aspartic acid			
Threonine			
Glutamine			



001674

Fig. 1. Inhibition of quinoidal chromogen formation from tyrosine and ClO_2 by iodide.

(I) The spectrum of tyrosine (0.25 mM) and ClO_2 (0.55 mM) in the absence of I^- , characterized by the absorbance of the quinoidal chromogen at $\lambda_1 = 496$ nm and the $\pi \rightarrow \pi^*$ transitional band of the aromatic ring of the unreacted tyrosine at $\lambda_2 = 298$ nm. (II) Iodide (0.833 mM) added to tyrosine (0.125 mM) before addition of ClO_2 (0.275 mM). The spectrum is characterized by the iodine absorption at $\lambda_3 = 348$ nm and that of unreacted tyrosine and iodinated tyrosines. (III) The U.V. spectrum of 3,5-diiodotyrosine,

TABLE III

ELECTRODE POTENTIALS*, EQUILIBRIUM CONSTANTS AND ELECTROMOTIVE FORCE FOR REDOX COUPLES BETWEEN IODIDE AND DRINKING WATER DISINFECTANTS

Redox couple				$E(V) \log K_{eq}^b$ EMF(V)*		
Products	Halide	Products	Disinfectant			
2.5 I_2	$5\text{I}^- - 5e^-$	$\text{Cl}^- + 2\text{H}_2\text{O}$	$\text{ClO}_2 + 5e^- + 4\text{H}^+$	-0.94	79.7	-1.07
I_2	$2\text{I}^- - 2e^-$	$\text{Cl}^- + \text{H}_2\text{O}$	$\text{HOCl} + 2e^- + \text{H}^+$	-0.95	32.3	-1.01
I_2	$2\text{I}^- - 2e^-$	$\text{Cl}^- + \text{OH}^-$	$\text{OCl}^- + 2e^- + \text{H}_2\text{O}$	-0.36	12.3	-0.42
I_2	$2\text{I}^- - 2e^-$	$\text{Cl}^- + \text{NH}_3 + \text{OH}^-$	$\text{HH}_2\text{Cl} + 2e^- + \text{H}_2\text{O}$	-0.21	7.2	-0.27

*Standard electrode potentials used:

$\text{I}_2 + 2e^- \rightleftharpoons 2\text{I}^-$	$E_0 = 0.54\text{V}$
$\text{OCl}^- + \text{H}_2\text{O} + 2e^- \rightleftharpoons \text{Cl}^- + \text{H}_2\text{O}$	$E_0 = 0.90\text{V}$
$\text{ClO}_2 + 5e^- + 4\text{H}^+ \rightleftharpoons \text{Cl}^- + 2\text{H}_2\text{O}$	$E_0 = 1.48\text{V}$
$\text{HOCl} + \text{H}^+ + 2e^- \rightleftharpoons \text{Cl}^- + \text{H}_2$	$E_0 = 1.49\text{V}$
$\text{NH}_2\text{Cl} + 2e^- + \text{H}_2\text{O} \rightleftharpoons \text{Cl}^- + \text{NH}_3 + \text{OH}^-$	$E_0 = 0.75\text{V}$

$K_{eq} = \frac{[\text{I}_2]}{[\text{I}^-]^2}$ computed from Nernst equation.

*Computed using $[\text{Ox}] = 1 \times 10^{-4}$ M, $[\text{I}^-]_{\text{gastric juice}} = 1 \times 10^{-4}$ M and $\text{EMF} = [E_{\text{anode}}] + (0.0591/n) \times \log [\text{Ox}] - [E_{\text{cathode}}] + (0.0591/n) \times \log [\text{Red}]$.

Radiation safety

All procedures using radio isotopes were conducted according to the radiation safety manual of the U.S. Environmental Protection Agency, A.W. Breiden Research Center, Cincinnati, OH.

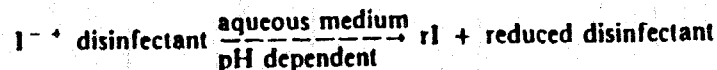
RESULTS

The iodination efficiency of nutrients in the presence of the three disinfectants listed in Table I, and those failing to react are listed in Table II. Fig. 1 shows combined spectra of the quinoidal tyrosine chromogen and its absence when iodide is present in the reaction mixture, and the spectral scans of 3,5-diiodotyrosine and 3-iodotyrosine are also shown.

DISCUSSION

EMF and equilibrium constants (K_{eq}) were computed using the Nernst equation for redox couples between disinfectants and I^- which are most likely to exist in gastric space following ingestion of disinfectants (Table III). These values are based on activity coefficients valid only for pure aqueous solutions; thus, they can be taken only as approximations of redox activities in a complex organic matrix. The disinfectant/halide couples, the ClO_2/I^- and the HOCl/I^- pairs stand out

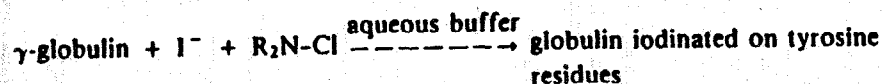
the others in terms of chemical potential. Thus, it is likely that the dominant reaction of ClO_2 (and possibly of the other disinfectants also) in the complex biochemical environment of the gastrointestinal tract is the oxidation of I^- to a reactive iodine species (ri):



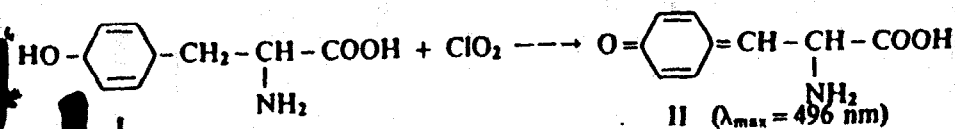
Subsequent chemical reactions of ri may follow a variety of pathways [3]:

- | | | |
|---|--------|--|
| (a) ri + olefins, fats | -----> | iodine addition across double bonds |
| (b) ri + PUFA | -----> | iodo-lactone ring formation and addition |
| (c) ri + olefins | -----> | iodohydrin formation |
| (d) ri + electron-rich aromatic or heterocyclic rings | -----> | iodine substitution |
| (e) ri + activated CH_2 group, e.g. ketones | -----> | iodine substitution |

An excellent example of the dominance of I^- oxidation in complex organic mixtures occurs in the radioiodination of antibodies and antigens. In these routinely performed reactions, a relatively strong oxidizing species such as chloramine-T or H_2O_2 reacts with I^- without destroying the sensitive tertiary structure manifest in hapten specificity and/or antigenicity of the protein, e.g.



In fact, to provide proof of the preferential oxidation of iodide by ClO_2 , we demonstrated by spectroscopic means (Fig. 1) that the purple chromogen (II) formed by the oxidation of tyrosine (I) by ClO_2 , a moiety frequently used for the spectral quantitation of ClO_2 (4) cannot be seen when I^- is present in excess.



lead, mono and diiodotyrosines are generated. Most of the compounds and complex biological substances listed in Table I possess structures or subunits, such as tyrosine within the globulin chain, which

cy of ClO_2 to induce iodination is in agreement with the relative magnitude of redox parameters. Exceptions are notable for HOCl , which in spite of its high calculated EMF than that of NH_2Cl , is a less effective iodinating agent for so substrates. This is plausibly due to the competitive tendency of HOCl to chlorinate organics rather than to oxidize I^- , a process not possible with NH_2Cl .

A large portion of nutrients which failed to bind iodide belong to molecular classes without functional groups capable of iodination, e.g., aliphatic amino acids, saturated fatty acids, etc., or those which reduce ri to I^- , such as cysteine, vitamin E (Table II).

Although the literature is largely devoid of information regarding iodine derivatives of the substances listed in Table I, a few hints are available to some of the structures. Previously it has been shown that iodination of arachidonic acid in the presence of lactoperoxidase/ H_2O_2 resulted in the formation of an iodo- δ -lactone and several iodinated isomers of eicosatetraenoic acid [5]. Initial chromatographic attempts on our part indicated that reaction mixtures containing 4-aminobenzoic acid and folic acid contained the known mono and diiodo isomers of 4-aminobenzoic acid.

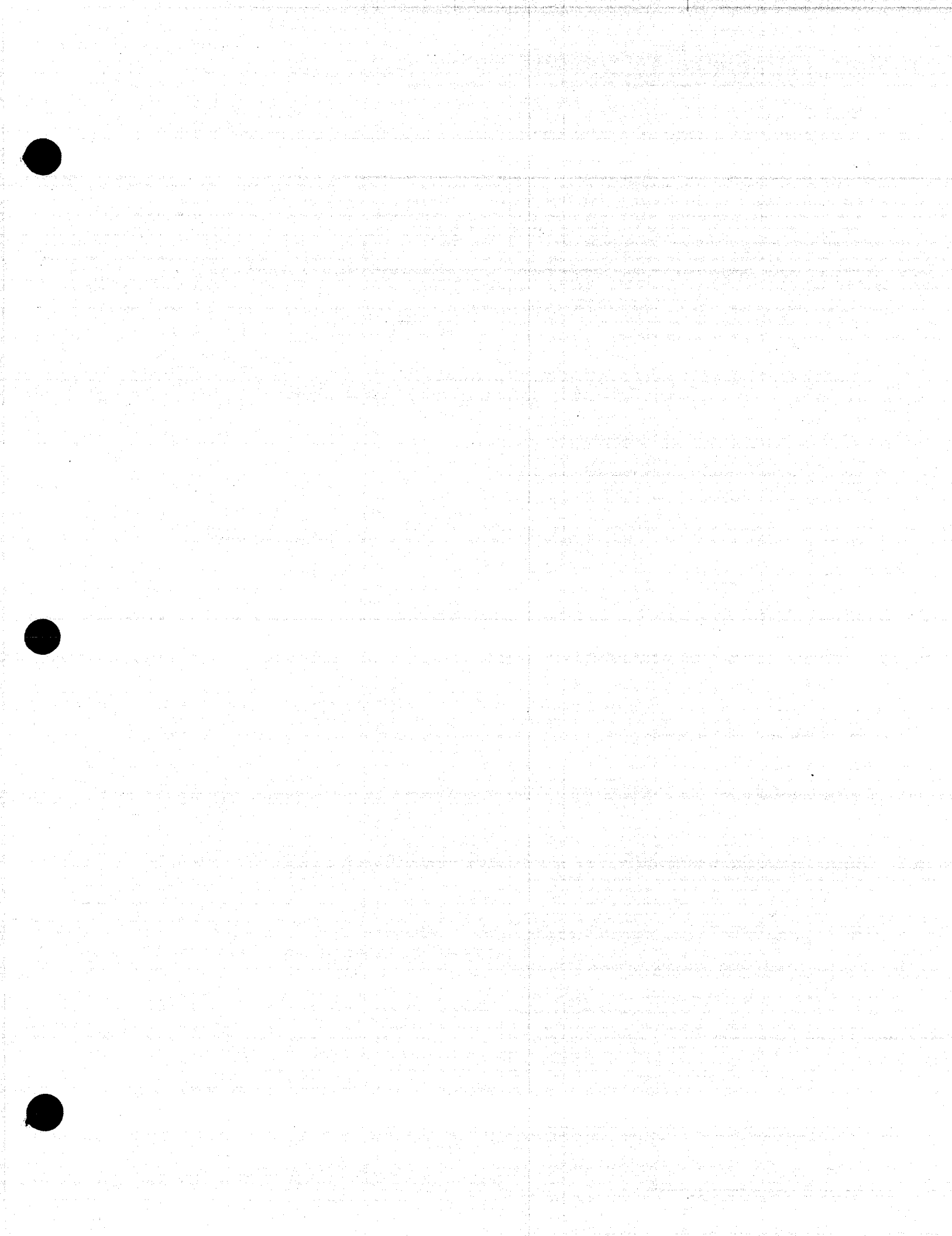
Presently we postulate that some of these iodinated molecules may have thyromimetic or thyroid inhibitory properties. Furthermore, such compounds may be also cytotoxic or have genotoxic/carcinogenic potential. Currently work in progress to identify the structures, in vivo formation, distribution, metabolic and biological activity of these compounds.

The research described in this article has been reviewed by the Health Effects Research Laboratory, United States Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

REFERENCES

- 1 R.M. Harrington, H. Shertzer and J.P. Bercz, Effects of ClO_2 on the absorption and distribution of dietary iodide in the rat, *Fundam. Appl. Toxicol.*, 5(4) (1985) 678-684.
- 2 J.P. Bercz, L. Jones, L. Garner, D. Murray, D.A. Ludwig and J. Boston, Subchronic toxicity of chlorine dioxide and related compounds in drinking water in the non-human primate, *Environ. Health Perspect.*, 46 (1982) 47-55.
- 3 A. Bayless and H. Zimmer, Preparation of C-I and C-I-X compounds, *Meth. Chim.*, 7 (1977) 28.
- 4 H.W. Hodgen and R.S. Ingols, Direct colorimetric method for the determination of chlorine dioxide in water, *Anal. Chem.*, 26(7) (1954) 1223-1226.
- 5 J.M. Boeynaems, D. Reagan and W.C. Hubbard, Lactoperoxidase-catalyzed iodination of arachidonic acid: formation of macrolides, *Lipids*, 16(4) (1981) 246-249.

001675





Wednesday
December 16, 1998

Federal Register

Part IV

Environmental Protection Agency

40 CFR Parts 9, 141, and 142
National Primary Drinking Water
Regulations: Disinfectants and
Disinfection Byproducts; Final Rule

001676



ENVIRONMENTAL PROTECTION AGENCY**40 CFR Parts 9, 141, and 142****[WH-FRL-8199-8]****RIN 2040-AB82****National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts****AGENCY:** Environmental Protection Agency (EPA).**ACTION:** Final rule.

SUMMARY: In this document, EPA is finalizing maximum residual disinfectant level goals (MRDLGs) for chlorine, chloramines, and chlorine dioxide; maximum contaminant level goals (MCLGs) for four trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform), two haloacetic acids (dichloroacetic acid and trichloroacetic acid), bromate, and chlorite; and National Primary Drinking Water Regulations (NPDWRs) for three disinfectants (chlorine, chloramines, and chlorine dioxide), two groups of organic disinfection byproducts (total trihalomethanes (TTHMs)—a sum of the four listed above, and haloacetic acids (HAA5)—a sum of the two listed above plus monochloroacetic acid and mono- and dibromoacetic acids), and two inorganic disinfection byproducts (chlorite and bromate). The NPDWRs consist of maximum residual disinfectant levels (MRDLs) or maximum contaminant levels (MCLs) or treatment techniques for these disinfectants and their byproducts. The NPDWRs also include monitoring, reporting, and public notification requirements for these compounds. This

document includes the best available technologies (BATs) upon which the MRDLs and MCLs are based. The set of regulations promulgated today is also known as the Stage 1 Disinfection Byproducts Rule (DBPR). EPA believes the implementation of the Stage 1 DBPR will reduce the levels of disinfectants and disinfection byproducts in drinking water supplies. The Agency believes the rule will provide public health protection for an additional 20 million households that were not previously covered by drinking water rules for disinfection byproducts. In addition, the rule will for the first time provide public health protection from exposure to haloacetic acids, chlorite (a major chlorine dioxide byproduct) and bromate (a major ozone byproduct).

The Stage 1 DBPR applies to public water systems that are community water systems (CWSs) and nontransient noncommunity water systems (NTNCWs) that treat their water with a chemical disinfectant for either primary or residual treatment. In addition, certain requirements for chlorine dioxide apply to transient noncommunity water systems (TNCWSs).

EFFECTIVE DATE: This regulation is effective February 16, 1999. Compliance dates for specific components of the rule are discussed in the Supplementary Information Section. The incorporation by reference of certain publications listed in today's rule is approved by the Director of the Federal Register as of February 16, 1999.

ADDRESSES: Public comments, the comment/response document, applicable Federal Register documents, other major supporting documents, and a copy of the index to the public docket for this rulemaking are available for

review at EPA's Drinking Water Docket: 401 M Street, SW., Washington, DC 20460 from 9 a.m. to 4 p.m., Eastern Standard Time, Monday through Friday, excluding legal holidays. For access to docket materials, please call 202/260-3027 to schedule an appointment and obtain the room number.

FOR FURTHER INFORMATION CONTACT: For general information contact, the Safe Drinking Water Hotline, Telephone (800) 426-4791. The Safe Drinking Water Hotline is open Monday through Friday, excluding Federal holidays, from 9:00 am to 5:30 pm Eastern Time. For technical inquiries, contact Tom Grubbs, Office of Ground Water and Drinking Water (MC 4607), U.S. Environmental Protection Agency, 401 M Street SW, Washington, DC 20460; telephone (202) 260-7270. For Regional contacts see **SUPPLEMENTARY INFORMATION**.

SUPPLEMENTARY INFORMATION: This regulation is effective 60 days after publication of Federal Register document for purposes of the Administrative Procedures Act and the Congressional Review Act. Compliance dates for specific components of the rule are discussed below. Solely for judicial review purposes, this final rule is promulgated as of 1 p.m. Eastern Time December 30, 1998, as provided in 40 CFR 23.7.

Regulated entities. Entities regulated by the Stage 1 DBPR are community and nontransient noncommunity water systems that add a disinfectant during any part of the treatment process including a residual disinfectant. In addition, certain provisions apply to transient noncommunity systems that use chlorine dioxide. Regulated categories and entities include:

Category	Examples of regulated entities
Industry	Community and nontransient noncommunity water systems that treat their water with a chemical disinfectant for either primary or residual treatment. In addition, certain requirements for chlorine dioxide apply to transient noncommunity water systems.
State, Local, Tribal, or Federal Governments.	Same as above.

001677

This table is not intended to be exhaustive, but rather provides a guide for readers regarding entities likely to be regulated by this action. This table lists the types of entities that EPA is now aware could potentially be regulated by this action. Other types of entities not listed in this table could also be regulated. To determine whether your facility is regulated by this action, you should carefully examine the

applicability criteria in § 141.130 of this rule. If you have questions regarding the applicability of this action to a particular entity, contact one of the persons listed in the preceding **FOR FURTHER INFORMATION CONTACT** section or the Regional contacts below.

Regional Contacts

- I. Kevin Reilly, Water Supply Section, JFK Federal Bldg., Room 203, Boston, MA 02203, (617) 565-3616
- II. Michael Lowy, Water Supply Section, 290 Broadway 24th Floor, New York, NY 10007-1866, (212) 637-3830
- III. Jason Gambatese, Drinking Water Section (3WM41), 1650 Arch Street, Philadelphia, PA 19103-2029, (215) 814-5759

0.08 mg/L for chlorite. The proposed MCLG was based on an RfD of 3 mg/kg/d estimated from a lowest-observed-adverse-effect-level (LOAEL) for neurodevelopmental effects identified in a rat study by Mobley et al. (1990). This determination was based on a weight of evidence evaluation of all the available data at that time (EPA, 1994d). An uncertainty factor of 1000 was used to account for inter- and intra-species differences in response to toxicity (a factor of 100) and to account for use of a LOAEL (a factor of 10).

The 1994 proposal included an MRDLG of 0.3 mg/L for chlorine dioxide. The proposed MRDLG was based on a RfD of 3 mg/kg/d estimated from a no-observed-adverse-effect-level (NOAEL) for developmental neurotoxicity identified from a rat study (Orme et al., 1985; EPA, 1994d). This determination was based on a weight of evidence evaluation of all available health data at that time (EPA, 1994a). An uncertainty factor of 300 was applied that was composed of a factor of 100 to account for inter- and intra-species differences in response to toxicity and a factor of 3 for lack of a two-generation reproductive study necessary to evaluate potential toxicity associated with lifetime exposure. To fill this important data gap, the CMA sponsored a two-generation reproductive study in rats (CMA, 1996).

As described in more detail in the 1998 NODA (EPA, 1998a), EPA reviewed the CMA study and completed an external peer review of the study (EPA, 1997d). In addition, EPA reassessed the noncancer health risk for chlorite and chlorine dioxide considering the new CMA study (EPA, 1998d). This reassessment was also peer reviewed (EPA, 1998d). Based on this reassessment, EPA requested comment in the 1998 NODA (EPA, 1998a) on changing the proposed MCLG for chlorite from 0.08 mg/L to 0.8 mg/L based on the NOAEL identified from the new CMA study which reinforced the concern for neurodevelopmental effects associated with short-term exposures.

EPA determined that the NOAEL for chlorite should be 35 ppm (3 mg/kg/d chlorite ion, rounded) based on a weight-of-evidence approach. The data considered to support the NOAEL are summarized in EPA (1998d) and included the CMA study as well as previous reports on developmental neurotoxicity and other adverse health effects (EPA, 1998d). EPA continues to believe, as stated in the 1998 NODA (EPA, 1998a), that the RfD for chlorite should be 0.03 mg/kg/d (NOAEL of 3 mg/kg/d with an uncertainty factor of 100) and that a MCLG of 0.8 mg/L is

appropriate. EPA has concluded that the RfD for chlorine dioxide should be 0.03 mg/L (NOAEL of 3 mg/kg/d with an uncertainty factor of 100) and that a MRDLG of 0.8 mg/L is appropriate.

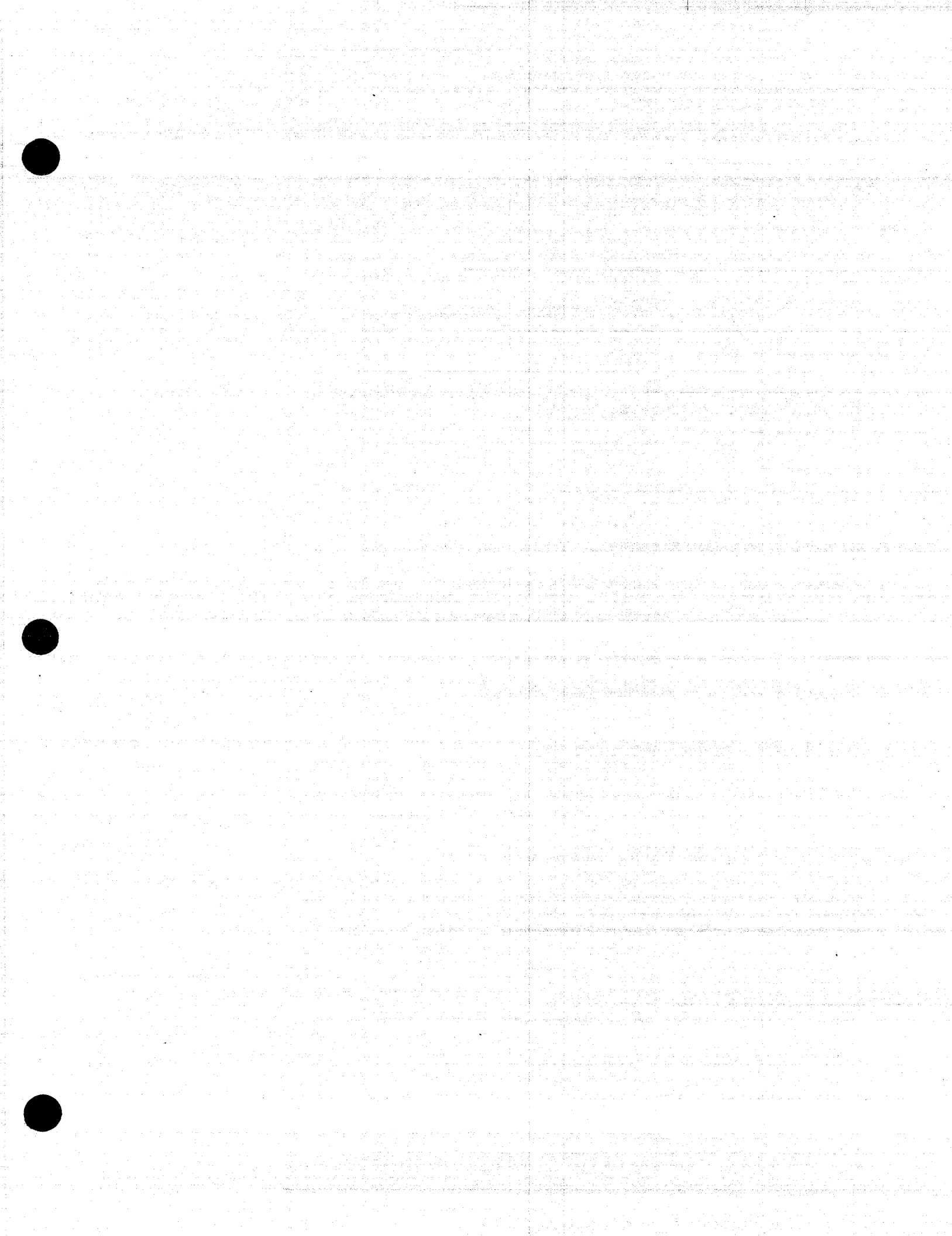
c. Summary of Comments. EPA received numerous comments on the 1994 proposal (EPA, 1994a) and 1998 NODA (EPA, 1998a). The major comment from the 1994 proposal was that reliance on the Mobley et al. (1990) study for the MCLG for chlorite and the Orme et al. (1985) study for chlorine dioxide were inappropriate and that the results from the CMA study must be evaluated before any conclusions on the MCLG for chlorite or chlorine dioxide could be drawn. In relation to the 1998 NODA, several commenters supported changing the MCLG for chlorite and MRDLG for chlorine dioxide while others were concerned that the science did not warrant a change in these values. The major comments submitted against raising the MCLG and MRDLG focused on several issues. First, one commenter argued that the 1000-fold uncertainty factor used for chlorite in the proposal should remain in place because the CMA study used to reduce the uncertainty factor was flawed. Second, several commenters indicated that the LOAEL should be set at the lowest dose level (35 ppm) because certain effects at the lowest dose tested may have been missed. Finally, some commenters argued that an additional safety factor should be included to protect children and drinking water consumption relative to the body weight of children should be used instead of the default assumption of 2 L per day and 70 kg adult body weight.

EPA agrees with commenters on the 1994 proposal that the results from the CMA should be factored into any final decision on the MCLG for chlorite and chlorine dioxide. As explained in more detail in the 1998 DBP NODA (EPA, 1998a), EPA considered the findings from the CMA study along with other available data to reach its conclusions regarding the MCLG and MRDLG for chlorite and chlorine dioxide.

EPA disagrees with the commenter who suggested that the 1000-fold uncertainty factor for chlorite should remain because the CMA study was flawed. The study design for the neurodevelopmental component of the CMA study was in accordance with EPA's testing guidelines at the time the study was initiated. EPA had previously reviewed the study protocol for the CMA neurotoxicity component and had approved the approach. While EPA initially had some questions regarding the design of the neurodevelopmental component of the study (Moser, 1997),

subsequent information submitted by the CMA provided clarification on certain aspects of the study design (CMA, 1998). EPA agrees that even with the clarifications that there are some limitations with the neurodevelopmental component of the CMA study. EPA believes that the neuropathology components of the CMA study were adequate. The functional operation battery had some shortcomings in that forelimb and hindlimb grip strength and foot splay were not evaluated. EPA believes the results from the motor activity component of the CMA study were difficult to interpret because of the high variability in controls. However, in its evaluation of the MCLG for chlorite and chlorine dioxide, EPA did not rely solely on the CMA study, but used a weight-of-evidence approach that included consideration of several studies. Thus, the shortcomings of one study are offset by the weight from other studies. EPA believes that the CMA study contributes to the weight-of-the-evidence. The studies by Orme et al. (1985), Mobley et al. (1990), and CMA (1996) support a NOAEL of 3 mg/kg/d based on neurodevelopmental effects (e.g., decreased exploratory, locomotor behavior, decreased brain weight). Furthermore, the CMA study was reviewed by outside scientists as well as by EPA scientists. EPA's re-assessment for chlorite and chlorine dioxide presented in the 1998 March NODA was reviewed internally and externally in accordance with EPA peer-review policy. The three outside experts who reviewed the Agency's assessment agreed with the NOAEL of 3 mg/kg/day and the derived RfD.

Finally, EPA disagrees that an additional safety factor should be applied to provide additional protection for children or that drinking water consumption relative to the body weight of children should be used in developing the MCLG. The MCLG and MRDLG presented for chlorite and chlorine dioxide are considered to be protective of susceptible groups, including children, given that the RfD is based on a NOAEL derived from developmental testing, which includes a two-generation reproductive study. A two-generation reproductive study evaluates the effects of chemicals on the entire developmental and reproductive life of the organism. Additionally, current methods for developing RfDs are designed to be protective for sensitive populations. In the case of chlorite and chlorine dioxide a factor of 10 was used to account for variability between the average human response and the





Reregistration Eligibility Document (RED)

PB92-180116

EN



Sodium and Calcium Hypochlorites

001679

REPORT DOCUMENTATION PAGE		1. REPORT NO.	PB92-180116	
4. Title and Subtitle <i>Sodium and Calcium Hypochlorite (A.E.D.)</i>			5. Report Date	
7. Author(s) EPA, Office of Pesticide Programs, Special Review & ReReg. Div.			8. Performing Organization Rept. No. 540/RS-92-193	
9. Performing Organization Name and Address U.S. Environmental Protection Agency Office of Pesticide Programs Special Review and Reregistration Division 401 M Street, S.W. Washington, D.C. 20460			10. Project/Task/Work Unit No.	
12. Sponsoring Organization Name and Address same as #9			11. Contract(C) or Grant(G) No. (C) (G)	
15. Supplementary Notes			13. Type of Report & Period Covered	
16. Abstract (Limit: 200 words)			14.	
<p>EPA is directed by the Federal Insecticide, Fungicide, and Rodenticide Act as amended in 1988 (FIFRA '88) to review all pesticide products containing active ingredients initially registered before November 1, 1984, and to reregister those products that have a substantially complete data base and do not pose unreasonable adverse effects to people or the environment. This pesticide reregistration program is to be completed by the late 1990's.</p> <p>The Reregistration Eligibility Document (or RED) discusses the scientific data and other information supporting EPA's regulatory conclusion that products containing a pesticide do not pose unreasonable risks when used as directed by Agency-approved labeling, and are eligible for reregistration.</p>				
17. Document Analysis a. Descriptors				
Pesticides, standards regulations, manufacturing, chemistry, toxicology, residues, ecology, path of pollutants.				
b. Identifiers/Open-Ended Terms				
c. COSATI Field/Group				
18. Availability Statement Publicly Available			19. Security Class (This Report) unclassified	21. No. of Pages 5
			20. Security Class (This Page) unclassified	22. Price

001680

Sodium and Calcium Hypochlorite

Summary of Requirements

For Products that were subject to the Standard the following are required: (Note: Data Call-In not required).

Within 90 Days of Receipt of this RED

- Submit a letter certifying that your product meets the criteria of the 1986 Standard.

Within 8 Months of Receipt of this RED

- Submit a completed Application for Reregistration (EPA Form 8570-1).
- Submit five copies of the label and labeling revised as specified by the RED and in accordance with current requirements.
- Submit two completed copies of the Confidential Statement of Formula (EPA Form 8570-4).
- Submit a completed Certification With Respect to Citation of Data (EPA Form 8570-31).

For Products that were not subject to the Standard the following are required:

Within 90 Days of Receipt of this RED

- Sign and submit both data call-in response forms attached to the DCI (Attachment B and C of the data call-in).

Within 8 Months of Receipt of this RED

- Submit a completed Application for Reregistration (EPA Form 8570-1).
- Submit five copies of the label and labeling revised as specified by the RED and in accordance with current requirements.
- Submit two completed copies of the Confidential Statement of Formula (EPA Form 8570-4).
- Submit a completed Certification With Respect to Citation of Data (EPA Form 8570-31).
- Submit the required data or references to data as specified by the RED/DCI.

001681



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

FEB 26 1992

CERTIFIED MAIL

Dear Registrant:

Enclosed is a Reregistration Eligibility Document (RED) for the pesticide active ingredients sodium and calcium hypochlorite. The RED is the Environmental Protection Agency's evaluation of the sodium and calcium hypochlorite data base and presents the Agency's conclusions on which uses are eligible for reregistration and under what conditions and requirements. Also enclosed is the Pesticide Reregistration Handbook which provides instructions to registrants on how to respond to any labeling and data requirements specified in the RED and how to reregister products.

The RED identifies outstanding product specific data requirements for end-use products and manufacturing-use products. These requirements are listed on the Requirements Status and Registrant's Response Form, which, along with the Data Call-In Response Form listing all of your company's products subject to the RED, is included as an Attachment. Instructions for completing both forms are contained in the RED package. All product specific data must be submitted or cited and found acceptable by EPA before a product can be reregistered.

The RED identifies any specific labeling requirements such as restricted use classification, groundwater hazard statements, endangered species precautions, etc., necessary for reregistration based on a review of the generic data for the active ingredient. In addition, in order to be reregistered, all product labeling must be in compliance with format and content labeling as described in 40 CFR 156.10 and all labeling changes imposed by Pesticide Registration (PR) Notices.

001682

The Pesticide Reregistration Handbook contains detailed instructions for compliance with the RED and must be followed carefully. There are several key points to remember in preparing your response to the RED:

[REDACTED]

Within 90 Days of Receipt of This Letter:

1. For each product which meets the criteria of the 1986 Registration Standard (i.e., contain only 5.25% to 12.5% sodium hypochlorite or 65% to 70% calcium hypochlorite as the sole active ingredient and only contains inerts within the limits specified in the Standard), you need only submit a letter certifying that your product meets these criteria.
2. For each product which does not meet the criteria of the 1986 Registration Standard (i.e., products for which the percent active ingredient or inerts fall outside the ranges specified in the 1986 Registration Standard, products with inerts added other than water and products containing additional active ingredients), you must complete, sign and submit both data call-in response forms attached to the RED (Attachment B and C).
3. EPA has created "batches" of products which are similar with respect to acute toxicity (Attachment D). If your product is listed in a "batch," you have the option of participating in the batch. If you wish to participate in a batch, you should consult with other registrants in the batch and agree on who will provide the data. Carefully follow the instructions in Attachment C to assure that one registrant is committing to provide the data while the others offer to share in the cost of those data. Of course, if you do not want to join the batch, you must commit to provide the data on your own.
4. No time extensions will be granted for submitting one of the two responses above. If EPA does not receive a response for a product, it may issue a Notice of Intent to Suspend.
5. Any requests for data waivers or time extensions to the 8-month deadline must be submitted as part of your 90-day response. Such requests will not be considered in the 8-month response.

Within 8 Months of the Date of This Letter:

001683

1. For each product, you must submit a completed Application for Reregistration (EPA Form 8570-1), five copies of the label and labeling revised as specified by the RED and in accordance with current requirements, two completed copies of the Confidential Statement of Formula (EPA Form 8570-4), a completed Certification With Respect to Citation of Data (EPA Form 8570-31) and data or references to data (this is needed only for products which do not meet the criteria of the 1986 Standard--see item 3 below).
-
-
-

2. For products which meet the criteria of the 1986 Standard, you will not submit or cite any data. Rather, EPA will review your CSF and determine whether or not it agrees with the certification you submitted after 90 days.

3. For products which do not meet the criteria of the 1986 Standard you must submit or cite the required data as part of the Application for Reregistration. For most products, you will probably be citing data which has already been submitted to EPA. In these cases, you must submit a list of the studies and the corresponding EPA identifier numbers. Before citing these studies, you must be sure that these data meet EPA's current acceptance criteria (Attachment E). If you submit data for the first time, be sure to follow P.R. Notice 86-5. Failure to adequately comply with the data requirements specified in the RED may result in the issuance of a Notice of Intent to Suspend a product.

4. When submitting labeling and a CSF for each product, you must comply with P.R. Notice 91-2 (Appendix D). That notice requires that the amount of active ingredients declared in the ingredient statement must be stated as the nominal concentration rather than the lower certified limit. You have two options for submitting a CSF: (1) accept the standard certified limits (see 40 CFR 158.175) or (2) provide certified limits that are supported by the analysis of five batches. If you pick the second option, you must submit or cite the data for the five batches along with a certification statement as described in 40 CFR 158.175(e).

When submitting your 90-day and 8-month responses for a product, address them to the Product Manager who is named below. Be sure to use the correct address and distribution code shown on page 6 of the Product Reregistration Handbook enclosed.

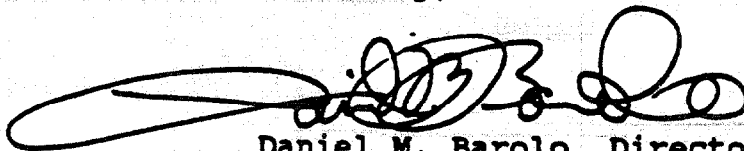
Questions on product-specific data requirements and labeling (both End-Use Products and Manufacturing-Use Products) should be directed to the Registration Division Product Manager Team for sodium and calcium hypochlorite, Ruth Douglas at (703) 305-7964. Questions on the generic database should be directed to Karen Samek, the Review Manager in the Special Review and Reregistration Division at (703) 308-8051.

The Agency is prepared to meet with any registrants who have questions about responding to the sodium and calcium hypochlorite RED. If you want to meet with the Agency, you must contact Ms. Douglas within two weeks of your receipt of the RED. The Agency

001684

intends to have one combined meeting with interested registrants. If there are any requests for such a meeting, the Agency will notify all registrants who requested a meeting of the location and date. Requests for a meeting will not extend the 90 day or 8 month response deadlines.

Sincerely,



Daniel M. Barolo, Director
Special Review and Reregistration Division

001685

**REREGISTRATION ELIGIBILITY DOCUMENT
SODIUM AND CALCIUM HYPOCHLORITE SALTS**

LIST A

CASE 0029

FEBRUARY 1992

**ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDE PROGRAMS
SPECIAL REVIEW AND REREGISTRATION DIVISION
WASHINGTON, D.C.**

001686



TABLE OF CONTENTS

	PAGE
GLOSSARY OF TERMS AND ABBREVIATIONS	1
EXECUTIVE SUMMARY	iii
I. INTRODUCTION	1
II. ACTIVE INGREDIENTS COVERED BY THE REREGISTRATION DECISION DOCUMENT	2
A. IDENTIFICATION OF ACTIVE INGREDIENT	2
B. USE PROFILE	2
C. REGULATORY HISTORY	3
III. AGENCY ASSESSMENT OF ACTIVE INGREDIENT	5
A. PRODUCT IDENTIFICATION	5
B. HUMAN HEALTH ASSESSMENT	5
1. TOXICOLOGY DATA	5
2. DIETARY EXPOSURE	6
a. RESIDUE DATA	6
b. TOLERANCE REASSESSMENT	7
3. OCCUPATIONAL AND RESIDENTIAL EXPOSURE	7
4. RISK ASSESSMENT	8
C. ENVIRONMENTAL ASSESSMENT	8
1. ECOLOGICAL EFFECTS ASSESSMENT	9
2. ENVIRONMENTAL FATE ASSESSMENT	10
IV. REREGISTRATION DECISION FOR SODIUM AND CALCIUM HYPOCHLORITE SALTS	12
A. DETERMINATION OF ELIGIBILITY	12
B. ADDITIONAL GENERIC DATA REQUIREMENTS	13
C. LABELING REQUIREMENTS	13

001687

V.	PRODUCT REREGISTRATION	14
A.	DETERMINATION OF ELIGIBILITY	14
B.	PRODUCT-SPECIFIC DATA REQUIREMENTS	15
C.	LABELING REQUIREMENTS	16
VI.	APPENDICES	
A.	APPENDIX A - DETAILED SPECIFIC USE SITES	19
B.	APPENDIX B - GENERIC DATA REQUIREMENTS FOR REREGISTRATION OF SODIUM AND CALCIUM HYPOCHLORITES AND DATA CITATIONS SUPPORTING REREGISTRATION	
1.	GUIDE TO APPENDIX B	26
2.	PRODUCT IDENTIFICATION (SODIUM HYPOCHLORITE)	27
3.	ECOLOGICAL EFFECTS (SODIUM HYPOCHLORITE)	28
4.	TOXICOLOGY (SODIUM HYPOCHLORITE)	29
5.	ENVIRONMENTAL FATE (SODIUM HYPOCHLORITE)	30
6.	PRODUCT IDENTIFICATION (CALCIUM HYPOCHLORITE)	31
7.	ECOLOGICAL EFFECTS (CALCIUM HYPOCHLORITE)	32
8.	TOXICOLOGY (CALCIUM HYPOCHLORITE)	33
9.	ENVIRONMENTAL FATE (CALCIUM HYPOCHLORITE)	34
B.	APPENDIX C - BIBLIOGRAPHY	
1.	GUIDE TO APPENDIX C	36
2.	BIBLIOGRAPHIC CITATIONS	38
D.	APPENDIX D - PR Notice 91-2	45
E.	APPENDIX E - DATA CALL-IN	

001688



GLOSSARY OF TERMS AND ABBREVIATIONS

ADI	Acceptable Daily Intake. Also known as the Reference Dose or RfD.
a.i.	Active Ingredient
ARC	Anticipated Residue Contribution
CAS	Chemical Abstracts Service
CSF	Confidential Statement of Formula
EEC	Estimated Environmental Concentration. The estimated pesticide concentration in an environment, such as a terrestrial ecosystem.
EP	End-Use Product
EPA	U.S. Environmental Protection Agency
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FFDCA	Federal Food, Drug, and Cosmetic Act
HDT	Highest Dose Tested
K+CWHR	Kernel plus Cob with Husk Removed
LC50	Median lethal concentration - a statistically derived concentration of a substance that can be expected to cause death in 50% of test animals. It is usually expressed as the weight of substance per weight or volume of water or feed, e.g., mg/l or ppm.
LD50	Median lethal dose - a statistically derived single dose that can be expected to cause death in 50% of the test animals, when administered by the route indicated (oral, dermal, inhalation). It is expressed as a weight of substance per unit weight of animal, e.g., mg/kg.
LDT	Lowest Dose Tested
LEL	Lowest Effect Level
MP	Manufacturing Use Product
MPI	Maximum Permissible Intake

GLOSSARY OF TERMS AND ABBREVIATIONS CONT'D

MRID	Master Record Identification (number). EPA's system of recording and tracking studies submitted to the Agency.
NPDES	National Pollutant Discharge Elimination System
NOEL	No Observed Effect Level
OPP	Office of Pesticide Programs
PADI	Provisional Acceptable Daily Intake
ppm	Parts per Million
RfD	Reference Dose
RS	Registration Standard
TMRC	Theoretical Maximum Residue Contribution

Executive Summary

The Environmental Protection Agency (referred to as "the Agency") first registered sodium and calcium hypochlorites as chlorinated inorganic disinfectants for use as sanitizers and disinfectants of surfaces, as disinfectants of water, and as chemicals to control microorganisms on certain foods and in certain industrial processes. All products which contain sodium and calcium hypochlorite as an active ingredient are eligible for reregistration except the uses on sugar syrup and raw sugar (the processed commodity). The uses on sugar syrup and raw sugar (the processed commodity) for calcium hypochlorite as well as for sodium hypochlorite are not eligible for reregistration without the acquiring of a food additive regulation from FDA.

In February 1986, the Agency issued a registration standard entitled "Guidance for the Reregistration of Pesticide Products Containing As the Active Ingredient Sodium and Calcium Hypochlorite Salts" (NTIS PB87-103222). The Registration Standard summarized the available data supporting the registration of sodium and calcium hypochlorite and determined that the data base was complete. No additional data were required for the generic data base in the 1986 Standard. The requirements listed in the Standard were cited only for those applicants who wanted to develop their own supporting data rather than rely upon and offer to pay compensation for the data cited in the Standard.

Recently, the Agency conducted a thorough review of the scientific data base and all relevant information supporting the reregistration of sodium and calcium hypochlorite and has determined that the data base is complete and is sufficient to allow the Agency to conduct a reasonable risk assessment. No further generic data are required. The data available to the Agency support the conclusion that the currently registered uses of sodium and calcium hypochlorites will not result in unreasonable adverse effects to the environment. No tolerances are required by the Agency to support the existing uses for the registered products because sodium hypochlorite is listed as GRAS (40 CFR 180.2) and calcium hypochlorite is exempt for the requirement of a tolerance under FFDCA sec. 408 (40 CFR 180.1054). It should be noted, however, that even though sodium hypochlorite is listed as GRAS (40 CFR 180.2) and calcium hypochlorite is exempt under Section 408 of the FFDCA from the requirements of a tolerance for use preharvest or postharvest on raw agricultural commodities, these exemptions do not cover the uses of sodium and calcium hypochlorite as food additives in or on processed foods which is regulated under Section 409 of the FFDCA. The 1986 Standard required registrants to obtain a food additive regulation for calcium hypochlorite in sugar syrup and raw sugar (the processed commodity) from FDA within 12 months from the date of issuance of the Standard or delete the claim from the appropriate product labeling. Since this regulation was not obtained, these uses must be deleted from the appropriate calcium,

as well as sodium hypochlorite product labeling within 8 months of the date of this document or be subject to enforcement action.

Accordingly, the Agency has determined that all products containing sodium and calcium hypochlorites as the active ingredient are eligible for reregistration except the uses on sugar syrup and raw sugar (the processed commodity) and will be reregistered when appropriate labeling and/or product specific data are submitted and/or cited. Those products which contain other active ingredients will be eligible for reregistration only when the other active ingredients are determined to be eligible for reregistration.

001692

I. INTRODUCTION

In 1988, the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) was amended to accelerate the reregistration of products with active ingredients registered prior to November 1, 1984. The amended Act provides a schedule for the reregistration process to be completed in nine years. There are five phases to the reregistration process. The first four phases of the process focus on identification of data requirements to support the reregistration of an active ingredient and the generation and submission of data to fulfill the requirements. The fifth phase is a review by the U.S. Environmental Protection Agency (referred to as "the Agency") of all data submitted to support reregistration.

Section 4 (g) (2) (A) of FIFRA states that in Phase 5 "the Administrator shall determine whether pesticides containing such active ingredient are eligible for reregistration" before calling in data on products and either reregistering products or taking "other appropriate regulatory action." Thus, reregistration involves a thorough review of the scientific data base underlying a pesticide's registration. The purpose of the Agency's review is to reassess the potential hazards arising from the currently registered uses of the pesticide; to determine the need for additional data on health and environmental effects; and to determine whether the pesticide meets the "no unreasonable adverse effects" criterion of FIFRA.

This document presents the Agency's decision regarding the reregistration of sodium and calcium hypochlorite. The document consists of five sections. Section I is this introduction. Section II describes sodium and calcium hypochlorite, its uses and regulatory history. Section III discusses the human health and environmental assessment based on the data available to the Agency. Section IV discusses the reregistration decision for sodium and calcium hypochlorite and Section V discusses product reregistration. Additional details concerning the Agency's review of available data are available on request.

001693

¹ EPA's reviews of specific reports and information on the set of registered uses considered for EPA's analyses may be obtained from: EPA, Freedom of Information, 400 St., S.W., Washington, D.C. 20460.

[REDACTED]

[REDACTED]

II. ACTIVE INGREDIENT COVERED BY THIS REREGISTRATION DECISION DOCUMENT

A. IDENTIFICATION OF ACTIVE INGREDIENT

The following active ingredients are covered by this Reregistration Eligibility Document:

Chemical Name: Sodium Hypochlorite

CAS Number: 7681-52-9

Office of Pesticide Programs Chemical Code Number: 014703

Empirical Formula: NaOCl

Chemical Name: Calcium Hypochlorite

CAS Number: 7778-54-3

Office of Pesticide Programs Chemical Code Number: 014701

Empirical Formula: CaOCl₂

B. USE PROFILE

Type of Pesticide: Chlorinated Inorganic Disinfectants

Pests Controlled: Bacteria, fungi, and slime forming algae that are pathogenic to man and animals

Registered Use Groups: (See Appendix A for detailed specific use sites).

For Sodium Hypochlorite:

Terrestrial Food Crop: citrus, apples, pears, quinces, stone fruits, cherries, nectarines, peaches, pecans, plums/prunes, melons, cucumbers, peppers, pimentos, tomatoes (postharvest application/seed treatment), brussels sprouts, cabbage, cauliflower, artichokes, lettuce, carrots, potatoes, radishes, sweetpotatoes, asparagus, mushrooms, onions, celery, peppers (seed treatment)

Terrestrial Feed Crop: citrus, apples, tomatoes (postharvest application/seed treatment)

Terrestrial Non-Food

Aquatic Food Crop

Aquatic Non-Food Residential

Aquatic Non-Food Outdoor
Aquatic Non-Food Industrial
Indoor Food
Indoor Non-Food
Indoor Residential
Indoor Medical
Residential Outdoor

For Calcium Hypochlorite

Terrestrial Food Crop: pecans (water treatment),
pecan (postharvest application to non-stored
commodities), pimentos (seed treatment), tomatoes
(seed treatment), potatoes and sweet potatoes
(postharvest application to non-stored
commodities), mushrooms (foliar or soil treatment),
vegetables or post harvest application to
vegetables crops, fruit or post harvest application
to fruit crops, seeds (Agricultural),
Terrestrial Feed Crop: seeds (Agricultural)
Terrestrial Non-Food Crop
Aquatic Food Crop
Aquatic Non-Food Industrial
Aquatic Non-Food Residential
Aquatic Non-Food Outdoor
Indoor Food
Indoor Non-Food
Indoor Residential
Indoor Medical
Residential Outdoor

Formulation Types Registered:

For Sodium Hypochlorite: Formulation intermediate,
granular, wettable powder, emulsifiable
concentrate, soluble concentrate, solution-ready to
use.

For Calcium Hypochlorite: Formulation intermediate,
dust, granular, pelleted/tabletted, wettable
powder, wettable powder/dust, soluble concentrate,
solution-ready to use.

C. REGULATORY HISTORY

Sodium and calcium hypochlorites are well known
compounds whose chemical and toxicological properties are
extensively documented in published literature and
studies submitted to the Agency. In February 1986, a
Registration Standard was issued for sodium and calcium

hypochlorite which summarized the available data supporting their registration. The standard concluded that no additional scientific data would be necessary to support the registration or reregistration of products which contain sodium hypochlorite from 5.25% to 12.5% or calcium hypochlorite from 65% to 70% as the only active ingredient, provided that no inert ingredients other than water were added and that Toxicity Category I labeling is used. The Registration Standard provided various options to applicants who wanted to register or reregister sodium or calcium hypochlorite products. The options implemented were:

- 1) Option I: Reliance on available data to support registration of toxicity category I products and adopt the generic labeling provided by the Agency. (This option was the "general registration" procedure designed to reduce processing time and costs to the Agency and registrants, while continuing to assure human and environmental protection. Only products containing 5.25%, 9.2%, 10%, or 12.5% sodium hypochlorite, or 65% calcium hypochlorite as the sole active ingredients were eligible for this option).
- 2) Option II: Either reliance on available data to support registration of toxicity category I products and submit their own labeling or development of data independently to support registration of toxicity category I products and submit their own specific labeling;
- 3) Option III: Development of product specific data independently by registrants to support lower toxicity categories II, III, or IV.

Manufacturing-use sodium hypochlorite and calcium hypochlorite products were defined by the standard as 12.5% and 65%, respectively; and product chemistry and acute toxicity data developed with these formulations also could be used to support end-use products of the same concentrations. The product chemistry and acute toxicity data developed with these formulations would also be extrapolated to support end-use concentrations of sodium hypochlorite down to 5.25%, since they are simply aqueous dilutions of the 12.5% manufacturing-use product.

001696



III. AGENCY ASSESSMENT OF ACTIVE INGREDIENT

The Agency has conducted a thorough review of the scientific data base for sodium and calcium hypochlorite. Based on the evaluation of these data, the Agency has no reason to change the major findings made in the 1986 document "Guidance for the Reregistration of Pesticide Products Containing as the Active Ingredient Sodium and Calcium Hypochlorite Salts". These findings are summarized below:

A. PRODUCT IDENTIFICATION

In the 1986 Registration Standard, no additional data were required on the product chemistry of sodium or calcium hypochlorite. The product chemistry data requirements listed in the standard were listed only for those applicants who wished to develop their own data rather than rely upon and offer to pay compensation for data cited in the standard. Calcium hypochlorite is a dull white powder with a strong odor of chlorine. It is a strong oxidant and has a critical ignition temperature of about 75° C. It decomposes violently above 150° C. This chemical has a molecular weight of 142.99. Sodium hypochlorite is produced as a greenish-yellow liquid with the smell of chlorine. It is inherently unstable and its decomposition is hastened principally by light, heat and trace metals. It is moderately corrosive and specific packaging is essential. Sodium hypochlorite is a strong oxidizing agent. This chemical has a molecular weight of 74.44 (anhydrous). The Agency has reevaluated the product chemistry data base and has determined that no additional data are required for reregistration for products that were subject to the standard.

B. HUMAN HEALTH ASSESSMENT

1. Toxicology Data Base

All current toxicological data requirements are satisfied. No further data were required in the 1986 registration standard (provided that toxicity category I labeling was used). The Agency has reevaluated the scientific data base for sodium and calcium hypochlorite and finds that the database for the purpose of human risk assessment is complete and no additional data are required. The available acute toxicity data are sufficient to address the acute toxicity risk to humans and the Agency has concluded that toxicity category I labeling is appropriate due to sodium and calcium hypochlorite's known potential for causing damage to

eyes. The Agency also concludes that no subchronic or chronic studies are needed. This conclusion is based on the simple chemical nature and structure of sodium and calcium hypochlorites and their high oxidative reactivity with organic matter which converts them readily into sodium chloride and calcium chloride. The human health concerns relative to these inorganic ions are well understood and the use of these chemicals will not add any additional calcium or sodium chloride burden for the users.

The Agency is aware of the potential risk concerning the formation of trihalomethanes, especially in drinking water, from the use of sodium and calcium hypochlorite. The Office of Drinking Water has addressed this risk by setting a maximum contaminant level of 100 ppb for trihalomethanes in drinking water. The Agency believes that this level is commensurate with an acceptable risk determination and limits the dietary exposure to hypochlorites.

2. Dietary Exposure

a. Residue Data

The February 1986 Guidance Document listed no residue chemistry data requirements for calcium or sodium hypochlorite. Under 40 CFR 180.1054, calcium hypochlorite is exempted from the requirement of a tolerance when used preharvest or postharvest in solution on all raw agricultural commodities. Sodium hypochlorite is considered to be Generally Recognized As Safe (GRAS) under 40 CFR 180.2. (The Agency intends to propose a specific exemption from the requirement of a tolerance for sodium hypochlorite on all raw agricultural commodities (RAC) under FFDCA sec. 408, and to delete the GRAS listing from 180.2). Based on this, no residue chemistry data are required for sodium or calcium hypochlorite under current scientific standards. There are no minor use concerns at present and there are no codex, Mexican, or Canadian MRL considerations with respect to sodium or calcium hypochlorite.

b. Tolerance Reassessment

Sodium hypochlorite is considered to be GRAS under 40 CFR 180.2. The Agency intends to propose a specific exemption from the requirement of a tolerance for sodium hypochlorite on all raw agricultural commodities (RAC) under FFDCA sec. 408, and to delete the GRAS listing from 180.2. An incidental food additive regulation allowing the use of sodium hypochlorite as a terminal sanitizing rinse on food processing equipment has been established (21 CFR 178.1010). Also, a food additive regulation permitting the use of sodium hypochlorite in washing or assisting in lye peeling of fruits and vegetables has been established (21 CFR 173.315) by the Food and Drug Administration (FDA). No new tolerances are necessary for the existing uses of sodium hypochlorite.

Calcium hypochlorite is exempted from the requirement of a tolerance under FFDCA sec. 408 (40 CFR 180.1054) when used preharvest or postharvest in solution on all raw agricultural commodities. The Agency has reevaluated this exemption and has determined that it is still appropriate. Also, an incidental food additive regulation allowing the use of calcium hypochlorite as a terminal sanitizing rinse on food processing equipment has been established (21 CFR 178.1010).

It should be noted, however, that even though sodium hypochlorite is considered to be GRAS and calcium hypochlorite is exempt under Section 408 of the FFDCA from the requirements of a tolerance for use preharvest or postharvest on raw agricultural commodities, these exemptions do not cover the uses of sodium and calcium hypochlorite as food additives in or on processed foods, which is regulated under Section 409 of the FFDCA. The 1986 Standard required registrants to obtain a food additive regulation for calcium hypochlorite in sugar syrup and raw sugar (the processed commodity) from FDA within 12 months from the date of issuance of the Standard or delete the claim from the appropriate product labeling. This food additive regulation has not been established for either sodium or calcium hypochlorite.

3. Occupational and Residential Exposure 001699

The 1986 Guidance Document for sodium and calcium hypochlorite did not require reentry or

mixer/loader/applicator exposure monitoring data. Sodium and calcium hypochlorite are chlorinated inorganic disinfectants registered for use in laundry, swimming pools, ponds, drinking water, and other water and wastewater systems, on food and non-food contact surfaces, and on various crops, including mushrooms (pins), potatoes, and sweet potatoes (postharvest). Based on current registered use patterns, the Agency has determined that the potential for post application exposure for sodium and calcium hypochlorite is minimal and therefore does not meet the Agency's exposure criteria for requirement of reentry or mixer/loader/applicator exposure monitoring data. Therefore, these data are not required to support the reregistration of sodium and calcium hypochlorite.

Based on the acute toxicity of sodium and calcium hypochlorite, label requirements for the use of protective clothing, including safety glasses or goggles and chemical-resistant gloves while handling end-use products containing sodium or calcium hypochlorite as the active ingredient remain as required in the 1986 Guidance Document. Reentry levels for application of sodium or calcium hypochlorite to swimming pools (3.0 ppm) and spas/hot tubs (5.0 ppm) and reentry intervals for spray/fog application to food and non-food contact surfaces (2 hour reentry interval following application) also remain as required in the 1986 Guidance Document.

4. Risk Assessment

Based on the above considerations concerning the toxicology profile and exposure scenarios for calcium and sodium hypochlorites it can be concluded that risks from chronic and subchronic exposure to low levels of calcium and sodium hypochlorites are minimal and without consequence on human health. Risks for acute exposure to high concentrations of calcium and sodium hypochlorites may be significant with respect to eye and skin injury but the Agency believes that these risks are sufficiently mitigated by adequate precautionary labeling requiring protection of eyes and skin while using calcium and sodium hypochlorites.

C. ENVIRONMENTAL ASSESSMENT

The environmental fate and ecological effects data requirements have been satisfied for all currently registered uses eligible for reregistration. In the 1986 Registration Standard, it was determined that the available fish and wildlife data were sufficient to characterize the acute toxicity risks to non-target

organisms and that no subchronic or chronic data were required. Many of these data requirements were fulfilled by the EPA Publication Ambient Water Quality Criteria for Chlorine by J. Tobler, et al; U.S. EPA, June 1981. Thus, no further environmental fate or ecological effects data were required.

The data cited in the Standard are discussed below. Upon reevaluation, the available data support the conclusion that the currently registered uses of sodium and calcium hypochlorite will not result in unreasonable adverse effects to the environment. As discussed in the Standard, the currently accepted uses that result in point source discharges of effluents containing sodium and calcium hypochlorites will continue to be regulated through issuance of National Pollutant Discharge Elimination System (NPDES) permits. Such permits are tailored to a specific site or point of discharge. The Agency has determined that the discharge amounts permitted by the NPDES permits, which are specific to each site, will not pose significant adverse effects on non-target organisms.

1. Ecological Effects Assessment

There are a number of scientifically sound data considered adequate to characterize the toxicity of the sodium and calcium hypochlorite salts. Results from the avian acute oral studies (MRID 00007276, 00007403, and 00007496) indicate that the sodium and calcium salts are low in toxicity to avian wildlife. The results from the avian subacute dietary studies (MRID 00007275, 00007278, 00007404, and 00007405) indicate that the sodium salt is practically non-toxic to upland game birds and waterfowl. Results from the fish acute toxicity studies (MRID 00007400, 00007495, 00008190, 00008191, and 00007401) indicate that the hypochlorite salts are highly toxic to freshwater fish. The acceptable studies on the acute toxicity to freshwater invertebrates (MRID 00007279, 00007402, 00007495, and 00019313) indicate that the hypochlorite salts are very highly toxic to freshwater invertebrates. Although these fish and aquatic invertebrate studies demonstrate high toxicity to sodium and calcium hypochlorite, the Agency believes that these risks are sufficiently mitigated by adequate precautionary labeling and the NPDES permit requirement. The results of these studies are listed below:

<u>Species</u>	<u>Test</u>	<u>Value</u>	<u>Toxicity</u>
Upland Game Birds	acute oral	LD ₅₀ 3474 mg/kg (Ca) LD ₅₀ >2510 mg/kg (Na)	Practically Non-toxic
Upland Game Birds and Waterfowl	Subacute Dietary	LC ₅₀ >5000 ppm (Na)	Practically Non-toxic
Cold Water Fish	acute toxicity	LC ₅₀ 0.132-1.35 ppm (96-hr) (hypochlorite salts)	Highly toxic freshwater fish
Warm Water Fish	acute toxicity	LC ₅₀ 0.28-2.1 ppm (96-hr) (hypochlorite salts)	Highly toxic freshwater fish
<u>Daphnia magna</u>	acute toxicity	LC ₅₀ 0.037-2.3 ppm (48-hr) (hypochlorite salts)	Very highly toxic to freshwater invertebrate

2. Environmental Fate Assessment

The February 1986 Guidance Document listed no environmental fate deficiencies for calcium or sodium hypochlorite. The environmental fate data requirements for the hypochlorite salts have been fulfilled by the document Ambient Water Quality Criteria for Chlorine (MRID 40911802), published by the Environmental Protection Agency. No further environmental fate data were required in the 1986 Guidance Document. After reevaluating the environmental fate data base, the Agency has determined that it will not require any additional environmental fate data. In aqueous media, sodium hypochlorite and calcium hypochlorite produce hypochlorous acid, hypochlorite ions, and hydronium ions, a reaction which is independent of the nature of the counter cation (i.e., sodium or calcium). The amount of hypochlorous acid, hypochlorite and hydronium ions present in solution depends on the pH of the medium. The data available indicate that the photolysis rate of calcium hypochlorite in aqueous solution increases with increasing light intensity. Calcium hypochlorite at 10 g/l has a half-life of 10-12 months and 4 months under diffused daylight and under diffused daylight with

intermittent direct sunlight, respectively. Seawater has a large capacity to consume hypochlorites. Sodium hypochlorite is expected to show a similar behavior. When sodium hypochlorite is added to seawater, residual chlorine levels declined rapidly in the first hour. The rapid initial decline was followed by a much slower and continuous decline in residual chlorine levels. The available data indicate that hypochlorites undergo reaction with bromide ions in seawater to form hypobromite. This reaction is rapid and appears to be complete within 2.5 minutes. Although hypobromite is acutely toxic to aquatic organisms, from a chronic viewpoint it does not appear to be toxic because it is highly volatile and will not persist in the aquatic environment. (Half-life is less than 96 hrs in water). The Agency believes that the risk of acute exposure to aquatic organisms is sufficiently mitigated by adequate precautionary labeling and the NDPEs permit requirement.

Although no exposure, bioaccumulation, or volatility data are available to quantitatively assess the potential for exposure of wildlife to the hypochlorites, the use patterns indicate that most exposure will occur in the aquatic environment, and that significant amounts of hypochlorites in the terrestrial environment will not occur.

The available data are considered sufficient to assess the environmental fate of the hypochlorite salts and the data support the conclusion that the currently registered uses of sodium and calcium hypochlorite will not result in unreasonable adverse effects to the environment.

IV. REREGISTRATION DECISION FOR ACTIVE INGREDIENT

A. DETERMINATION OF ELIGIBILITY

Section 4 (g) (2) (A) of FIFRA calls for the Agency to determine, after submission of relevant data concerning an active ingredient, whether products containing the active ingredient are eligible for reregistration. The Agency has previously identified and required the submission of the generic (i.e., active ingredient specific) data required to support reregistration of products containing sodium or calcium hypochlorite as an active ingredient. The Agency has completed its review of these generic data, and has determined that the data are sufficient to support reregistration of products containing sodium or calcium hypochlorite. Appendix B identifies the generic data requirements that the Agency reviewed as part of its determination of reregistration eligibility of sodium and calcium hypochlorites, and lists the submitted studies that the Agency found acceptable.

The data identified in Appendix B are sufficient to allow the Agency to conduct a reasonable risk assessment for the registered uses of sodium and calcium hypochlorite. The data available to the Agency support the conclusion that the registered uses of sodium and calcium hypochlorite will not result in unreasonable adverse effects to the environment. The Agency has determined that all products containing sodium and calcium hypochlorites as the active ingredient are eligible for reregistration except the uses on sugar syrup and raw sugar (the processed commodity). The uses on sugar syrup and raw sugar (the processed commodity) for sodium and calcium hypochlorite are not eligible for reregistration without the acquiring of a food additive regulation from FDA. (See Section III(B)(2)(b) of this document). Since this regulation was not obtained, these uses must be deleted from the appropriate product labeling within 8 months of the date of this document or be subject to enforcement action. The reregistration of particular products is addressed in section V of this document ("Product Registration").

The Agency made its reregistration eligibility determination based upon the target data base required for reregistration, the current guidelines for conducting acceptable studies to generate such data, and the data identified in Appendix B. Although the Agency has found that products containing sodium and calcium hypochlorite are eligible for reregistration, it should be understood that the Agency may take appropriate regulatory action, and/or require the submission of additional data to support reregistration of products containing sodium or calcium hypochlorite, if new information comes to the Agency's attention or if the data requirements for registration (or the guidelines for

generating such data) change.

B. ADDITIONAL GENERIC DATA REQUIREMENTS

The generic data base supporting the reregistration of products containing sodium or calcium hypochlorites has been reviewed and determined to be complete for reregistration. No further generic data are required.

C. LABELING REQUIREMENTS FOR MANUFACTURING-USE PRODUCTS CONTAINING SODIUM OR CALCIUM HYPOCHLORITES

1. The labels and labeling of all products must comply with EPA's current regulations and requirements. Follow the instructions in the Product Reregistration Handbook with respect to labels and labeling. Any product label which allows both manufacturing and end use must be amended to specify only manufacturing or end use. In this situation, if a registrant amends his/her label to specify manufacturing use only and wishes to retain end use registration, he/she must apply for a separate end-use product registration.
2. Based on the reviews of the generic data, the following additional label statements are required:
 - a. In the directions for use, the following statement must appear:

"Formulators using this product are responsible for obtaining EPA registration of their formulated products."
 - b. In the directions for use, the following statement regarding acceptable use patterns must appear:

"For formulation into end-use products intended only for (list acceptable sites)."
 - c. The following Environmental Hazard statement is required for any use that results in discharge into the aquatic environment:

"This pesticide is toxic to fish and aquatic organisms. Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or public waters unless this product is specifically identified and addressed in an NPDES permit. Do not discharge effluent containing this product to sewer systems without previously

001705

notifying the sewage treatment plant authority. For guidance contact your State Water Board or Regional Office of the EPA."

- d. Because of the corrosive nature of sodium and calcium hypochlorite and the potential for severe eye and skin damage from accidental spills of these chemicals, EPA is requiring that the Statement of Practical Treatment appear on the front panel of all products which have been assigned toxicity category I for eye and/or skin effects.
- e. The "If Swallowed" statement in the statement of practical treatment must read as follows:

"IF SWALLOWED, drink large amounts of water. DO NOT induce vomiting. Call a physician or poison control center immediately."

V. PRODUCT REREGISTRATION

A. DETERMINATION OF ELIGIBILITY

Based on the reviews of the generic data for the active ingredients, sodium and calcium hypochlorites, the products containing this active ingredient are eligible for reregistration. Section 4(g)(2)(b) of FIFRA calls for the Agency to obtain any needed product-specific data regarding the pesticide after a determination of eligibility has been made. The Agency will review these data when they have been submitted and/or cited and determine whether to reregister individual products.

For products that meet the criteria of the 1986 standard and were registered or reregistered under option I (the "general Registration" procedure) (the registrant relied on available data to support registration of Toxicity Category I products and adopted the generic labeling provided by the Agency), or option II (the registrant either relied on available data to support registration of Toxicity Category I products and submitted their own specific labeling or developed data independently to support registration of toxicity category I products and submitted their own specific labeling), the Agency is requiring that labels reflecting the changes stated within this document and CSFs be submitted within 8 months of receipt of this document. Upon receipt and approval of revised labels and CSFs, these products, will be reregistered under section 4(g).

001706

For products that do not meet the criteria of the 1986 Standard, (i.e. products whose concentrations of the a.i. fall outside the range specified by the standard for sodium hypochlorite 5.25% - 12.5% and for calcium hypochlorite 65% - 70%; products with intentionally added inert ingredients other than water; and products which are mixtures with other active ingredients), the Agency is requiring that the registrants either submit product specific data or cite previously submitted data to support their registrations and submit revised labeling and CPSS within 8 months of receipt of this document before the products will be considered for reregistration. After reviewing these data and the revised labels, the Agency will determine whether to reregister each product based on whether or not it meets the requirements in section 3(c)(5) of the Federal Insecticide, Fungicide, and Rodenticide Act. Those products which contain other active ingredients will be eligible for reregistration only when the other active ingredients are determined to be eligible for reregistration.

While the Agency will continue to register sodium and calcium hypochlorite products as discussed above under the provisions of the February 1986 Registration Standard, EPA does not plan to issue further amendments to that document. Consequently, EPA will no longer consider amendments to general registration (Series 20,000) labeling for the purpose of adding uses or language inconsistent with that Standard. Applicants who wish approval for such amendments must apply for a new product registration and will be assigned a conventional registration number upon acceptance.

B. PRODUCT SPECIFIC DATA REQUIREMENTS

The product-specific data requirements are stated in the attached appendices. For those products that were not subject to the 1986 Registration Standard (which include those products whose concentrations of the a.i. fall outside the range covered by the standard for sodium hypochlorite 5.25% - 12.5% and for calcium hypochlorite 65% - 70%; those products with additional inert ingredients other than water, and those products which are mixtures with other active ingredients) the registrant is responsible for either submitting data or citing previous data he submitted to support his registrations. Registrants of products which were subject to the 1986 registration standard do not need to submit or cite data since they did so already in complying with that standard.

001707

The Agency has decided to continue its current policy of waiving the product-by-product efficacy data requirement normally levied on sanitizers and disinfectants for sodium and calcium hypochlorite formulations. The Agency has concluded that the published literature data can reasonably be extrapolated to the full range of these products.

C. LABELING REQUIREMENTS FOR END-USE PRODUCTS CONTAINING SODIUM OR CALCIUM HYPOCHLORITE

1. The labels and labeling of all products must comply with EPA's current regulations and requirements. Follow the instructions in the Product Reregistration Handbook with respect to labels and labeling. Any product label which allows both manufacturing and end use must be amended to specify only manufacturing or end use. In this situation, if a registrant amends his label to specify end-use registration and wishes to retain manufacturing use registration, he must apply for a separate manufacturing use product registration.
2. Because of the corrosive nature of sodium and calcium hypochlorite and the potential for severe eye and skin damage from accidental spills of these chemicals, EPA is requiring that the Statement of Practical Treatment appear on the front panel of all products which have been assigned toxicity category I for eye and/or skin effects.
3. The "If Swallowed" statement must read as follows:

"IF SWALLOWED, drink large amounts of water. DO NOT induce vomiting. Call a physician or poison control center immediately."
4. The 1986 Registration Standard stated that applicants whose product labeling contains use in sugar syrup and raw sugar must obtain a food additive regulation to support these uses as required by the provisions of the Federal Food Drug and Cosmetic Act (21 CFR 173 Subpart D -Specific Usage Additives). Since this regulation was not obtained, registrants whose product labeling contains the food additive claim for calcium hypochlorite in sugar syrup and raw sugar (the processed commodity) must delete this claim from the appropriate calcium, as well as sodium hypochlorite labeling within 8 months of the date

of this document or be subject to enforcement action.

5. The following Environmental Hazard statement is required for any use that results in discharge into the aquatic environment:

"This pesticide is toxic to fish and aquatic organisms. Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or public waters unless this product is specifically identified and addressed in an NPDES permit. Do not discharge effluent containing this product to sewer systems without previously notifying the sewage treatment plant authority. For guidance contact your State Water Board or Regional Office of the EPA."